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**EUROPEAN CONFERENCE  
ON ADVANCED MATERIALS  
AND PROCESSES**

NOVEMBER 22 - 24, 1989  
AACHEN, FEDERAL REPUBLIC OF GERMANY

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**ABSTRACTS**

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FEDERATION OF EUROPEAN MATERIALS SOCIETIES

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**ABSTRACTS**

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The individual abstracts of oral and poster presentations  
are published unchanged as submitted by the authors.

Sequence of these abstracts corresponds  
to the conference programme.



→ Federation of European Materials Societies  
held its conference on November 20-24, 1989  
at AACHEN, Federal Republic of Germany. The  
following topics were discussed:

Plenary Sessions 1, 2, 3, 4

**Workshops**

- COST 503, Powder Metallurgy
- COST 504, Advanced Casting and Solidification Technology

**Symposium A: Advanced Processing**

- I Forging
- II Casting
- III Powder Technology

**Symposium B I: Special Materials**

- I Superalloys
- II Steels
- III Composites and Ceramics

**Symposium B II: Special Materials**

- I Biomaterials

**Symposium C: High Technology Applications**

- I Materials Science in Electronic Packaging and Device Technology
- II Ceramic Packaging
- III Materials, Trends and Processing in Advanced Packaging

**Joint Symposium C + D: High Technology Applications/Basic Phenomena**

- I Interfaces in Packaging
- II Thin Film Packaging and Polymer/Metal Interfaces
- III Metal/Ceramic Interfaces and Packaging

**Symposium D: Basic Phenomena**

- I Interface Reactions

**Symposium E: Innovative Analysis Methods**

- I Scanning Tunneling and Force Microscopy
- II Acoustic Scanning Microscopy

Poster Group I.-XXIII.

**Accession For**

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See programme, page 13.

**"Which materials will be successful in the future"**

Yves FARGE

PECHINEY - 23, rue Balzac 75008 - PARIS - FRANCE

Materials constitute a diffuse (or horizontal) technology which plays an essential role in our technical system. Every breakthrough in materials has induced revolutions in our industrial system and strong modifications of our culture : steel and public transportation, aluminium and aircraft industry, silicon and communications, ...

Each of these revolutions has been a combination of different factors : technical factors related with new functions brought by the material, cost factors often related to a reduction of prices of existing functions or with new functions, cultural factors related to the ability of our societies to develop and use these materials. Each of these revolutions has been very long over periods of more than twenty years.

In coming years, it is difficult to foresee a new fundamental revolution in the field of materials but a progressive evolution can be predicted related with the improvement of existing materials and their combinations. The important functions in the future will be the following :

- improved structural functions and lightening
- reduction of the energy content
- recyclability related with waste and availability
- lifetime, especially corrosion

These functions concerne mass production representing more than 90 % of the market of materials (housing, packaging, automotive industry, ...)

The consumption of such materials could largely increase with the industrialisation of developing countries.

More specific functions will continue to be developed for special applications and some examples will be given in the field of electronics of chemical engineering.

A good equilibrium must be kept between mass production and specific materials to avoid the technical challenge for itself and to meet the needs of our civilisation.

See programme, page 13.

## BIOMATERIALS FOR BONE AND JOINT REPLACEMENT

W. Bonfield

Dept. of Materials, Queen Mary & Westfield College, London, UK

The total replacement of arthritic joints with an artificial system consisting of various bio-inert metals, polymers and ceramics has allowed a dramatic advance in orthopaedic surgery. Approximately 500.000 patients per year on a world-wide basis are now benefitting from total hip arthroplasty, but the resulting lifetime of the prosthesis is finite and although acceptable for elderly patients is less than satisfactory for younger patients. The failure mechanism is not in general related to fracture of the prosthesis itself, but to associated bone remodelling producing loosening of the femoral stem or acetabular cup. It is demonstrated that the interaction between the implant materials and cortical bone is a critical factor controlling bone remodelling. Recent developments to innovate novel synthetic biomaterials with analogous properties to those of cortical bone are considered, with particular reference to hydroxyapatite reinforced polymer composites, which produce bone apposition rather than bone resorption around an implant and offer the prospect of an enhanced prosthesis lifetime.

See programme, page 13.

#### HIGH TEMPERATURE MATERIALS - THE BROAD SCENE

G W Meetham  
Rolls-Royce plc

Thermal energy is crucial in many major technology areas including electrical and mechanical power generation, materials processing, environment control and the dissipation of other energy forms. Thus high temperature technology is of crucial importance in industries such as primary metal and non-metal production, material processing, chemical engineering, transportation etc. For many of these industries, the price of fuel is a major element of overall operating cost and materials that allow operation at high temperature are essential for industrial competitiveness.

High temperature materials are considered in the paper on the basis of the ratio of their maximum use temperature to melting temperature rather than simply on the basis of maximum use temperature. This definition thus includes aluminium titanium and nickel alloys, steels, refractory metals and various non metallic materials. Operating environments involve a wide spectrum of mechanical and chemical conditions. Thus some materials are used solely because of their corrosion resistance, some solely because of their strength and others because of a combination of strength and corrosion resistance. Some are used solely for thermal insulation. In the highest temperature applications above about 4000 C thermal ablative material must be used.

The paper discusses the various types of high temperature materials, their key characteristics and applications and their relationship with one another.

See programme, page 13.

## TRENDS IN HIGH PERFORMANCE INTEGRATED CIRCUIT PACKAGING

Barry C. Johnson  
E. I. du Pont de Nemours and Company  
Central Research and Development  
Wilmington, Delaware, USA

High performance integrated circuits from the basic building blocks of modern electronic systems that are designed to process ever larger numbers of electrical signals at greater signal velocity and fidelity. In such applications, each circuit must be packaged in order to provide it with necessary mechanical support, environmental protection, electrical interconnection and thermal cooling. However, the combination of increasing circuit complexity, customization, size, speed and heat flux is leading to a crisis in packaging technology<sup>(1,2)</sup>. It is anticipated that the continuing evolution of high performance circuits and systems will soon be severely limited by the package and interconnect characteristics, rather than by the devices on the semiconductor chip.

The intent of this paper is to provide a brief overview of the future trends in high performance integrated circuit packaging. The approach is to: (1) present the forecasted trends in relevant circuit performance characteristics; (2) discuss the impact of these characteristics on current chip- and board-level packaging methods; and (3) present new packaging concepts that are emerging as potential solutions to the developing circuit-package performance gap<sup>(3)</sup>. Particular emphasis will be placed on the changing package design guidelines and material requirements.

### REFERENCES:

1. J. H. Hohl and B. C. Johnson, "Challenges of a Vintage 1994 CMOS Logic Chip," Proc. Custom Integrated Circuits Conf., 23.1.1 (May 16-19, 1988).
2. B. C. Johnson, "Overview of Chip-Level Packaging," to be published in Electronic Materials Handbook, Volume 1, ASM International (1989).
3. C. A. Neugebauer and R. O. Carlson, "Comparison of Wafer Scale Integration with VLSI Packaging Approaches," IEEE Trans. Comp., Hybrids, Manuf. Technol., CHMT-10, 184 (1987).

See programme, page 14.

## KINETIC AND THERMODYNAMIC INSTABILITIES IN THIN FILM REACTIONS

Ulrich M. Gösele

School of Engineering  
Duke University  
Durham, NC 27706, USA

Modern materials science is increasingly concerned with thin films and interfaces especially in the area of microelectronics. The present paper will first deal with binary bilayer and multilayer thin film diffusion couples. In these diffusion couples generally not all of the phases predicted by the equilibrium phase diagrams are present. The concept of a kinetic instability of these phases is discussed. It is shown that the first nucleating phase has to exceed a critical thickness before a second phase can start to grow. The concept of a "critical thickness" is then extended to solid state amorphization in which non-equilibrium phases grow first in certain diffusion couples. This case is treated in terms of the maximum rate of decrease in Gibbs' free energy.

About 20Å thick SiO<sub>2</sub> layers sandwiched between two silicon wafers are produced via direct silicon wafer bonding. The thermodynamic structural instabilities occurring in such a system will be discussed, as well as how these instabilities can be avoided by an appropriate rotational misorientation of the two wafers involved in the bonding.

III-V compound superlattices are thermodynamically unstable, but generally the extremely low self-diffusion coefficients in these materials prevent disordering of the superlattices. The final part deals with impurity-diffusion-induced disordering of such superlattices and explanation of the observed self-diffusion enhancements by up to 12 orders of magnitude.

See programme, page 14.

## **Microscopy of Surfaces**

*Gerhard Ertl*

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Faradayweg 4-6, D-1000 Berlin 33, W. Germany

Information on the structure of surfaces may be obtained by applying indirect (e.g. diffraction) techniques or by direct microscopic imaging. This lecture will present an overview about recent developments in a few selected areas which are mainly related to properties of clean metal surfaces and their interactions with gases. Imaging electrons, emitted from a surface which is irradiated either with slow electrons or with UV photons, forms the basis of low energy electron microscopy (LEEM) and photoemission electron microscopy (PEEM), respectively, which techniques are particularly suited for investigating surface defects. Scanning photoemission microscopy (SPM) uses UV light focussed onto a small spot ( $\sim 1 \mu$ ) of the surface whose position is continuously scanned in x-y-directions while the yield of emitted electrons is collected without electron optical devices. Resolution down to atomic dimensions is reached with the scanning tunneling microscope (STM), even with densely packed metal surfaces, such as Al(111). Applications of these techniques will be illustrated by several examples.

See programme, page 14.

OPPORTUNITIES FOR MATERIALS RESEARCH IN EC FUNDED PROGRAMMES

A. GARCIA ARROYO  
COMMISSION OF THE EUROPEAN COMMUNITIES  
BRUSSELS

The Single European Act, signed in 1987, provides the platform for a common scientific policy to strengthen the scientific and technological basis of European industry. The objectives are to encourage the industry to become more competitive at an international level whilst at the same time speeding up the establishment of the large market that the EC has taken as its target for 1992. The instrument for pursuing this mandate is the Framework Programme, a multi-annual approach, which lays down the objectives, priorities and overall R & T D (Research and Technological Development) budget. The present Framework Programme (1987-1991) has a budget of 5396 Mio ECU.

Community research is focussed on those areas where the European dimension plays a significant role - research beyond the financial and human resources of a single member state or where it is essential to make full use of the complementary know-how and expertise available in Europe. A typical example of such EC activities is in the area of advanced materials, which have an enormous impact on all industrial sectors. This research is mainly covered by the Brite/Euram and Science programmes but is also treated in relation to specific requirements in other programmes like Esprit, Joule, Steel R & D, Bridge, etc.

In the most recent call for proposals under Brite/Euram more than 200 projects out of 645 were related to advanced materials with a total cost of 466 Mio ECU. About 1000 industrial enterprises, universities and research institutes from all 12 member states are involved.

The different measures which can be taken by the EC in stimulating and supporting R & T D activities such as shared cost activities, coordinated actions, feasibility awards, sectorial grants etc. will be presented by means of some examples.



See programme, page 14..

**COST 501: ADVANCED MATERIALS FOR POWER ENGINEERING COMPONENTS**

T B Gibbons

Division of Materials Applications

NATIONAL PHYSICAL LABORATORY

Teddington TW11 0LW, UK

The project has recently entered a second round and builds on the considerable experience developed in the earlier COST project, COST 50, on gas turbine materials and involves similar principles of concerted action. Thus the participants benefit by work-sharing to reduce the overall costs incurred in pre-competitive research in materials for high technology industries.

In the second round of the Project the work has been targetted on the needs of industry with well-defined objectives and fully integrated work programmes. The overall scope of the Project will be described in general terms and the coordination and management arrangements described. The significance of the work in the wider international context will be discussed.

See programme, page 14.

### **COST 503: A Concerted European Action in the Field of Powder Metallurgy**

R. Stickler  
University of Vienna, A

Powder Metallurgy has been identified as a key industrial technology where collaboration on critical research issues would increase the competitiveness of European companies in exploiting the technical potential for efficient near-net-shape manufacture with significant advantages in energy, materials and costs. The consequent expansion of the market for innovative cost-effective products should benefit not only large users and suppliers, but also to create opportunities for smaller specialized companies. In the European countries more than 100 industrial and research organisations are actively engaged in powder metallurgical processing, technological developments to improve quality, costs and productivity factors, and to increase the range of available materials and property data.

To achieve these goals it appeared essential to have a vigorous underpinning research program, coordinating many expert inputs and providing means of sharing costs and risks. For this reason a group of experts urged the implementation of a concerted R&D action within the framework of COST. A Declaration of Understanding for the action COST 503 "Powder Metallurgy" was signed in 1982. In response to a Call for Proposals more than 60 replies were received. Following a critical evaluation by an international expert committee 53 proposals were graded acceptable and recommendations to support these projects were issued to the national authorities of A, B, CH, D, DK, S, SF, and UK. The projects could be classified in three subgroups organized by coordinators in the fields of light metals and alloys, iron-based alloys, and hard materials.

During this first round of COST 503 (1985-1988) a fruitful international collaboration has been established between partners from industry, research institutes and universities. Several themes of wide-spread relevance have been identified and extensive groups of collaborative projects with important technological objectives have been initiated. The results of this concerted projects are documented in unclassified final reports which demonstrate that this collaboration provided effective means of information transfer.

At the end of this first round the opinion of the project leaders was assessed and the results of the work rationalized. As a result of the overwhelmingly positive replies it was decided to continue COST 503 for a second round, in order to exploit the enthusiasm of collaboration and the considerable research potential which has been created after less than 3 years of work. An extension appeared desirable to ensure the industrial valorisation of advanced research projects. This second round of COST 503 was initiated in 1988 with a working period of 3 years. Altogether 36 collaborative projects in the fields of hard materials, Al-based and Fe-based alloys from A, B, CH, D, DK, F, L, S, SF and UK are now in progress.

See programme, page 14.

## ***COST 504***

### ***ADVANCED CASTING AND SOLIDIFICATION TECHNOLOGY***

W. Kurz  
Lausanne

This research program is intended to improve the competitiveness of the foundry industry through the full exploitation of the potential of casting and solidification processes. Collaboration is taking place in the following fields:

- **advanced solidification processes** and techniques which improve the quality and performance of castings
- **dedicated computer software** allowing optimization and control of casting processes
- **new casting materials**, for example, metal matrix composites
- **process control**
- **properties for design**

The program, including 42 projects from 10 european countries, is in the middle of its second three years stage. The total budget of this second stage is approx. 14 Mio ECU corresponding to a total of more than 200 man-years. 43% of the projects are performed in industry, 31% in government or contract research laboratories and 26% in universities. The distribution of projects shows that the research is oriented towards both applications and more fundamental aspects.

In the paper, some results will be discussed which relate to numerical modelling of solidification, to improvement and control of product quality as well as to fibre-reinforced aluminium alloy castings.

See programme, page 15.

### Fatigue and Fracture of Advanced PM-Al Alloys

M.J.Couper\*), R.Schäfer\*\*), G.R.D.Shrimpton\*\*\*) and B.Weiss+)

The objectives of this collaborative effort involved the selection of suitable PM-Al alloys and to develop processing routes for these alloys to achieve superior strength and fatigue properties, both at room and elevated temperatures. The candidate PM-materials should be used for manufacturing automotive and aerospace components with properties comparable or exceeding those of conventionally processed parts. Three mechanically alloyed PM-Al materials with extremely fine grain size stabilized by ultrafine dispersoids were extensively evaluated, i.e. Al 9021 (Al-1.5Mg - 4Cu), Al 9052 (Al-4Mg) and Al 905-XL (Al-4Mg -1.5Li). Selected tests were also carried out with specimens of the PM-alloy Al 2618 (Al-Cu-Mg-Fe-Ni) and of a rapidly solidified powder of an Al-Fe-Mo alloy.

Several processing modifications were selected to optimize the mechanical properties. As base line data tensile and creep properties up to 180 C were determined. Special emphasis was placed on the investigation of HCF, LCF and fatigue crack growth behavior. The microstructure of the materials was characterized by LM and SEM methods.

The investigations revealed that internal defects occasional present in the specimens sensitively affect the mechanical properties, in particular the fatigue behavior. The magnitude of the detrimental effects was found to depend on the nature, size and distribution of the microstructural inhomogeneities. The results confirm that components of PM-Al alloys can be manufactured with excellent mechanical properties as long as homogenous material with a controlled distribution of defects smaller than a critical size is available for processing.

\*) ABB, Baden, CH

\*\*) IABG, Ottobrunn, D

\*\*\*) IEPL-INCO, Birmingham, UK

+) University of Vienna, A

See programme, page 15.

### **Processing and Properties of Rapidly Solidified Al Alloys**

M.J.Couper \*), M.Hohman\*\*), P.Schwellinger \*\*\*) and S.Savage+)

The aim of this cooperation was to increase the high temperature strength of aluminum alloys by advanced processing techniques. The main activity of this working group concentrated on the development and evaluation of materials prepared from various Al/Fe base alloy powders produced by the rapid solidification method. Inert gas atomization with argon and nitrogen were carried out to produce larger quantities of Al-8Fe-2Mo powder with particle size distributions of 80% below 50um and solidification rates above  $10^5$ K/sec. For comparison, smaller quantities of powders of similar composition were prepared by ultrasonic gas atomization in pressurized helium.

The powders were consolidated by extrusion to round bars. Novel degassing and extrusion processes have been investigated as well as the development of microstructure during consolidation. The microstructure and mechanical properties of the materials were evaluated before and after forging into components. Emphasis in evaluation was put on fatigue, creep and fracture properties.

The results have shown the importance of powder quality, the unsuitability of coarse slowly-cooled atomized powders, and have helped to demonstrate the optimum alloy system. The collaborative nature of the work is expected to lead to an accelerated acceptance and use of this new class of materials.

\*) ABB, Baden, CH    \*\*) Leybold-Heraeus GmbH, Hanau, D

\*\*) AluSuisse, Neuhausen, CH    +) SIMR, Stockholm, S

See programme, page 15.

## **The Influence of Trace Impurities on Technology and Properties of Hard Materials**

H. M. Ortner\*)

The aim, structure and most interesting results of a successful international cooperation concerning the influence of important trace impurities such as Ca, Al, Si, P and S on the production and final properties of hard metals are presented. The following institutions took part in these investigations:

- \* Metallwerk Plansee GmbH, Reutte, A: H.M.Ortner, P.Wilhartitz, in cooperation with the Institute for Analytical Chemistry, Technical University of Vienna, A: M. Grasserbauer, A.Virag, G.Friedbacher
- \* Institute of Chemical Technology, Technical University of Vienna, A: B.Lux, W.D.Schubert
- \* Fraunhofer Institute for Non-destructive Testing, Saarbrücken, D: K.Goebbels
- \* Montanwerke Walter GmbH, Tübingen, D: E.Kübel
- \* Fraunhofer Institute for Applied Materials Research, Bremen, D: H.Weiss, V.Schlett
- \* H.C.Starck, Goslar, D: H.Tulhoff, E.J.Martin
- \* Swedish Institute for Metal Research, S: V.Almquist, U.Gustavsson, B.Lehtinen, A.Nordgren
- \* AB Sandvik Coromant, S: B.Uhrenius, H.Brandrup-Wognsen
- \* Institute of Process Metallurgy, Helsinki University of Technology, SF: H.Manninen

Never before, to our knowledge, has this problem been studied in depth with such a wide variety of techniques including e.g. TEM, SIMS, sintering under controlled atmospheres, large scale thermodynamic equilibrium calculations etc. and by such a large international joint endeavour.

\*) Metallwerk Plansee GmbH, Reutte, A

See programme, page 15.

### **Hard Ceramics: A Successful Cooperation**

K.Weiss\*)

A short resumé of the structure, the goals, and the results of the first round of the COST-503 action in the field of hard ceramics will be presented. It will be made clear that the close and efficient european cooperation was the heart of the remarkable progress which was achieved. It will be made equally clear that this cooperation has to continue undiminished if a breakthrough to industrial applications is to be achieved.

\*) Hilti AG, Schaan, CH

See programme, page 15.

## **Development of Powder Metallurgical Roller Bearings for Large Constructions**

D.Pohl\*) and O.Kohlbacher\*\*)

Roller bearings for large constructions, such as bridges, require rolls consisting of a tough core material coated with a high-strength, hard and corrosion resistant surface layer. At present such rolls are being produced by weld deposition of a hardenable steel, e.g. X40Cr13, on a cylinder of a tough steel, e.g. 34CrNiMo6. Defects in the weld deposit seriously affect the properties of such composites.

The objective of present investigation involved a feasibility study of producing superior rolls combining a surface material manufactured from metal powder, compacted and diffusion joined to the core material by a HIP procedure. During the initial phase of this study an understanding of the important parameters of diffusion joining was achieved. Based on this experience actual components (130mm diameter, 250mm long, thickness of surface layer 20mm) were produced during a second working period, with various combinations of surface and core materials.

Non-destructive inspection has shown that the diffusion zone is continuous and free of defects. Loading tests indicated a much superior load bearing capacity of the PM-composite rolls compared to weld deposits. Further evaluation work is in progress.

\*) SHW, Wasseraalfingen, D

\*\*) Böhler GmbH, Kapfenberg,



See programme, page 15.

#### Development of Sintered Connecting Rods for Automotive Engines

K.Lipp<sup>1)</sup>, K.Richter<sup>2)</sup>, R.Lawcock<sup>3)</sup>, G.Schlieper<sup>4)</sup>, C.M.Sonsino<sup>1)</sup>,  
J.Tengzelius<sup>5)</sup>, D.Whittaker<sup>3)</sup>

The well known substitution of forged automotive connecting rods by cast iron in the early sixties and the fact that PM-steels in notched conditions and at densities above  $7.0 \text{ g/cm}^3$  can reach similar fatigue performances as wrought and cast materials encouraged the initiation of this European cooperative project with the following objectives:

- \* design of a PM connecting rod for automotive engines,
- \* generation of material data relevant to design considerations,
- \* design exercise in accordance with stress distribution, material properties and tooling restrictions,
- \* production by an economic single-step sintering technique with subsequent heat treatment,
- \* achievement of weight uniformity, required fatigue strength and cost savings.

To realize these requirements within a given time-frame the various tasks were assigned within the international collaboration, the design frame for a selected combustion engine was provided by a car manufacturer.

After preliminary finite-element calculations ten connecting rods were machined from pressed and sintered blanks using the material Fe-1.5Cu-0.6C with a density of  $6.9 \text{ g/cm}^3$ . Strain analyses using strain gauges indicated an agreement with the results of these calculations and highlighted those areas of the connecting rods which need to be optimized.

The general aim to achieve a fatigue performance of the PM rods comparable with conventional processed rods was in principle reached. Increases in fatigue performance by higher densities, improved homogeneity of density and a better starting material appear feasible to obtain a higher security margin against scatter due to manufacturing. Optimization of the interference between gudgeon pin and bore hole in the small end of the rod, together with thermal or mechanical surface treatments, offer further possibilities to increase the fatigue strength. These investigations are presently in progress.

1) LBF, Darmstadt, D, 2) Opel AG, Rüsselsheim, D,

3) GKN Technology, Wolverhampton, UK, 5) Högans AB, Högans, S

See programme, page 16.

**Numerical Modelling of Heat Transfer at Interfaces:  
Finite Element Approaches, Testing and Examples**

W. Schäfer, MAGMA Gießereitechnologie GmbH, Aachen, FRG

F. Hediger, Gießerei-Institut der RWTH, Aachen, FRG

A. Bührig-Polaczek, Gießerei-Institut der RWTH, Aachen, FRG

**Abstract** — Since the beginning of numerical simulation of macroscopic solidification systems, modelling of heat transfer at interfaces has been an important aspect. The aim of this paper is to present the development of heat transfer models implemented into a Finite Element code. The accuracy of each model is examined. In particular, the effects of the models on calculated temperature distribution in shape castings are evaluated.

See programme, page 16.

SIMULATION OF MOLDFILLING AND TEMPERATUREDISTRIBUTION IN A  
CASTING

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N-7034 Trondheim,  
NORWAY

The finite difference program FLOW-3D from Flow Science Inc. in Los Alamos has been utilized to calculate the metalflow of an aluminium alloy into a simple box-like cavity with a core. The temperaturedistribution is affected by the heat transfer in the gating system and in the mold cavity. This is also included in the model.

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### Phase Stability Diagram of Ternary Aluminium Alloy Systems

A. Roósz and H.E. Exner

From the equilibrium phase diagram the phases present in alloy solidified with an infinitely slow cooling rate can be found. Alloys solidified under practical conditions (cooling rate:  $10^{-1} - 10^2$  K/s) in technical castings processes will usually contain one or more nonequilibrium phases. Phase equilibrium can only be established if the solidified sample is annealed, usually for extended times at temperatures close to solidus in order to dissolve nonequilibrium phases.

Computer simulations for dendrite solidification of ternary alloys have been performed to calculate the amount of nonequilibrium phases in aluminium-rich Al-Cu-Mg alloys. The results compared favourably with measurements for five compositions ranging from 3 to 5 wt% Cu and 0.5 to 1.35 wt% Mg solidified at four solidification rates in the range between 1 and 20 K/s. The results are used for constructing a diagram which shows the phases present in alloys solidified at cooling rates in the range of technical relevance. It is suggested that this type of phase stability diagrams is useful in casting practice.

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## MODELLING OF SOLIDIFICATION OF NODULAR CAST IRON

M. RAPPAZ, J. D. RICHOSZ AND PH. THÉVOZ

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Ecole Polytechnique Fédérale de Lausanne  
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SWITZERLAND

Although the solidification of nodular cast iron is of great technical interest, some uncertainties still remain as far as the basic mechanisms of growth are concerned. It is believed that grain growth is primarily controlled by the diffusion of carbon atoms from the surrounding liquid to the central graphite nodule, through the austenite shell. The growth kinetics which have been derived for such eutectics are based upon several assumptions<sup>[1,2]</sup>: no contribution of solute diffusion in the liquid, stationary concentration profile within the austenite shell, and, in one model<sup>[2]</sup>, a constant ratio of the graphite nodule and austenite shell radii. However the relationships, between the growth rate of the grain interface and the undercooling, which are deduced in this way seem to be unable to reproduce experimental nodule size measurements and cooling curves<sup>[1,3]</sup>.

The present study investigates more carefully some of the underlying assumptions of growth models for nodular cast iron. The general equations of solute conservation have been derived for the two cases of complete and no-complete mixing of carbon atoms in the liquid, and these equations are compared with existing theories. Firstly, the assumptions of a stationary solute concentration in the austenite shell has been studied. For that purpose, the non-stationary solute concentration profile has been calculated, at each time step, by using a Finite Difference Method (FDM). The results of such calculations are not significantly different to those obtained using a stationary profile, thus validating the hypothesis of stationarity. Secondly, it has been demonstrated that solute diffusion in the liquid cannot be neglected in the early stages of growth. Furthermore, the ratio of the graphite nodule and the austenite shell radii is shown to vary substantially at the beginning of solidification. Thirdly, the growth kinetics obtained from a solute conservation analysis have been integrated into a general microscopic model for solidification which includes nucleation and grain impingement. It is shown that, since the growth kinetic is grain radius dependent, the time at which the grains are nucleated has a strong influence upon the calculated cooling curves, for a given final grain size. Finally, the simulation results are compared with experimental data, and fairly good agreement is obtained; providing that the "correct" nucleation law is used.

1. K. C. Su, I. Ohnaka, I. Yamauchi and T. Fukusako, *Computer simulation of nodular cast iron*, in *The Physical Metallurgy of Cast Iron*, Ed. H. Fredriksson and M. Hillert (North Holland, MRS Symp. Proc., Vol. 34, 1985), p. 181.
2. S. H. Wetterfall, H. Fredriksson and M. Hillert, *Solidification process of nodular cast iron*, J. Iron Steel Inst., May 1972, p. 323.
3. D. M. Stefanescu and C. Kanetkar, *Computer modeling of the solidification of eutectic alloys: comparison of various models for eutectic growth of cast iron*, in *State of the Art of Computer Simulation of Casting and Solidification Processes*, Ed. H. Fredriksson (Les Editions de Physique, 1986), p. 255.

See programme, page 16.

# MODELLING OF CAST IRON MICROSTRUCTURE

Dr F. MAMPAEY

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A simulation method has been developed which allows to calculate the eutectic cell count in lamellar graphite cast iron. This is realized by incorporating nucleation phenomena and grain growth while solving the heat transfer equation by conduction. Three original approaches feature this method : a numerical technique to treat the release of latent heat, an assumption regarding the distribution of heterogeneous nuclei and the study of the grain impingement effect by the Monte Carlo method.

The release of latent heat is governed by the relation of the growth velocity of the lamellar graphite eutectic as a function of the supercooling. A new finite difference technique enables to solve this equation simultaneously with the heat transfer equation in an implicit way. For the nucleation it is assumed that a new grain with a critical radius will only be formed if a solid particle is present in the melt having a flat substrate of minimal width. The width of all particle planes acting as heterogeneous nuclei is supposed to have a normal distribution.

Simulation results based on this approach are in line with experimental data of both inoculated and uninoculated cast iron poured in different massivities giving cell counts between 8 and 4500 / cm<sup>2</sup>. The simulated solidification morphology accords with the experimental one obtained by quenching. This verification is more accurate than comparing experimental and simulated cooling curves.

See programme, page 16.

#### Nucleation of graphite particles in grey and S.G. cast irons

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It is now experimentally well established that nucleation of graphite particles in inoculated cast irons occurs over a large temperature interval. This led to the assumption that there must exist a wide distribution of the sites for nucleation. With the aim of simulating the eutectic reaction of cast irons, a few proposals have been made for taking into account in calculations a continuous distribution of sites with undercooling <sup>1-3</sup>). Calculations showed clearly that there is an important competition between nucleation and growth for thermal conditions similar to usual casting conditions <sup>2</sup>).

It has been recently proposed <sup>4</sup>) to use the distribution law for the nucleation sites derived experimentally by Oldfield <sup>2</sup>), after weighting it by the volume fraction  $g^l$  of residual liquid. This gives the following variation of the number of activated sites  $dN_v$  during a slight decrease of the temperature  $dT$  in the solidification interval :

$$dN_v = A \cdot \Delta T_{eut} \cdot g^l \cdot dT$$

where  $\Delta T_{eut}$  refers to the temperature difference with respect to the equilibrium temperature for the beginning of the eutectic reaction.

A is a constant related to the efficiency of the inoculation : this single parameter characterizes a given melt preparation, it can be modified from one casting to another, for example due to different inoculation treatment or to fading. This law has been introduced in a numerical model for the simulation of the eutectic reaction of S.G. cast iron and was successfully applied to the prediction of the evolution of the volume number of graphite nodules and solidification kinetics of directionally solidified samples <sup>4</sup>).

The present paper is intended to discuss the possible physical background of the empirical law proposed by Oldfield and its application to S.G. as well as grey cast irons. Given a simple shape for the exogeneous particles acting as nucleation sites with their size as a variable, the nucleation rate will be expressed according to the classical steady-state theory for heterogeneous nucleation. When assuming a size distribution of the particles it is then possible to predict the variation of the number of activated nuclei with undercooling. This approach gives rise to the possibility of describing fading of the nucleation treatment.

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See programme, page 16.

## COMPUTER SIMULATIONS OF STRUCTURE AND MECHANICAL PROPERTIES OF NODULAR CAST IRON

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Nodular cast-iron castings are more and more used due to good mechanical properties, good castability and low price. The properties of nodular cast-iron castings are depending on the way it was produced and influenced by the metallurgy, cooling rate and transformation kinetics. Computer simulations have been made to predict mechanical properties related to solidification and solid state transformation structure in different cooling rates and influence of Si-content. The solidification structure has been calculated by using nucleation and growth laws. The solid state transformations are also using nucleation and growth laws. The parameters used in the calculations have been evaluated from experimental data. The calculations of heat transfer, structure formation and mechanical properties are integrated to a FEM-calculation program.



See programme, page 17.

### Microstructural Modelling of Near Net Forgings

R.W. Evans

The savings in material costs which result from near net shape forgings is particularly important in the aerospace industry where high strength nickel and titanium alloys are very expensive. In addition, the much reduced machining costs have helped to encourage near net shape methods. However, in many cases it is critical to achieve the correct metallurgical structure in the finished piece and this can often be achieved only by trial and error methods. The overall process becomes much more efficient if the forming process and metallurgical structure development can be modelled together prior to production trials.

Such modelling has two important aspects. A mechanical algorithm is required which not only allows an accurate prediction of initial flow but also permits the inclusion of thermal coupling for those processes which are not isothermal. In addition it is known that structural evolution is strongly connected to current temperatures and strain rates as well as the overall deformation history (e.g. accumulated strain patterns). This complex modelling exercise is gradually being solved and this paper discusses the various options that are currently available. These include elastic-plastic and visco-plastic analysis by finite element methods. The critical feature of these methods is that they require precise constitutive equations. Such equations are not simply relationships between stress, strain, strain rate and temperature. They also contain within themselves the key to microstructure development. The paper presents several possible procedures and illustrates the results which can be obtained for a variety of different forging processes.

See programme, page 17.

**CRITICAL ASPECTS OF THERMOMECHANICAL PROCESSING IN  
AL/TI PRECISION FORGING MANUFACTURE**

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Precision forgings in aluminum and titanium alloys are a cost efficient method of part manufacture for aerospace applications. Thermomechanical processing (TMP) techniques are an important aspect of the manufacturing process in order to capture superior mechanical properties in the final product. Enabling technologies including hot die/isothermal forging and computer controlled forging and secondary processing are being exploited to capture unique TMP methods for precision Al/Ti shapes .

For high strength 2XXX and 7XXX aluminum alloy forgings, TMP based upon an optimization of the traditional isothermal forging process to enhance fabricability, as demonstrated by significant reductions in unit pressures necessary to achieve complex forged shapes, are presented. Further, selected TMP based upon optimized forging process conditions and unique thermal treatments may be exploited to provide superior combination of properties in the final product. Reviewed are the effects of such TMP on alloys 7X75 and 7X50, which may demonstrate either higher toughness at equivalent electrical conductivity and stress corrosion resistance or alternatively significantly, up to 15%, higher strength with some necessary tradeoff in toughness and stress corrosion resistance. Finally, the effects of unrecrystallized microstructures, as may be achieved with selected TMP, on second tier properties such as fatigue and fatigue crack growth resistance will also be discussed.

The effects of controlled forging process conditions and unique TMP techniques on the fabricability and final microstructures and mechanical properties of selected titanium alloys in precision shapes are also presented. For the metastable  $\beta$  alloy Ti-10V-2Fe-3Al, that now finds wide application in precision titanium airframe forgings, selected combinations of forging process conditions are shown to be important enablers in the manufacture of precision shapes. Combination of selected forging process conditions with controlled thermal treatments are demonstrated to provide successful manipulation of the strength-toughness relationship in this alloy and result in enhanced final microstructures that facilitate capture of the alloy's superior fatigue characteristics. Finally, critical TMP of a high strength, high modulus emerging  $\alpha + \beta$  alloy Ti-6Al-2Sn-2Zr-2Cr-2Mo-0.25Si in precision and conventional forgings is reviewed to realize superior fatigue crack growth resistance and rationalized in terms of the microstructure achieved.

See programme, page 17.

IMPROVED MICROSTRUCTURE AND PROPERTIES  
OF Ti-10V-2Fe-3Al TITANIUM ALLOY  
THROUGH ISOTHERMAL FORGING

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Ti-10V-2Fe-3Al is a near-beta titanium alloy designed to be used in airframe structural forgings. It possesses a better hardenability and heat-treatability than alpha-beta alloys.

The aim of this collaborative programme is to define the process parameters that could give the optimum combination of strength, ductility and fracture toughness. The alloy has been isothermally forged either in the beta or alpha + beta field at different strain rates. The amount of forging reduction was varied between 0% and 160%. Solution treatments were performed in the beta or alpha+ beta field. A same ageing treatment was chosen for all conditions.

The alloy exhibits a coarse microstructure after a beta solution treatment whatever the forging temperature or the amount of reduction may be. The elongation to rupture is very low ( $\leq 1\%$ ).

On the opposite, a high ductility can be achieved with an alpha+beta solution treatment. However, a minimum deformation of 40% is required to obtain an acceptable elongation to rupture ( $\leq 5\%$ ). The increase in ductility at high reduction levels is due, in the case of beta forging, to a dynamic recrystallization leading to a refinement of the beta grain size and, in the case of alpha+ beta forging, to the formation of a fine recrystallized microstructure after solution treatment.

Isothermal beta forging followed by an alpha+beta solution treatment promotes the best overall properties. In that conditions, Ti-10V-2Fe-3Al offers a significant advantage over alpha-beta alloys, like Ti-6Al-4V.

See programme, page 17.

The Application of Finite Element Modelling  
to Isothermal Forging

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The uniform temperature maintained in the workpiece and the dies during isothermal forging gives much better process control than is possible with conventional metal working operations. The dimensional accuracy of the process is better as well as being more reproducible while the deformation conditions can be manipulated to give controlled microstructural development. The technique is, however, expensive and as a consequence is restricted to high value components. It is, therefore, advantageous to have a reliable method for simulating the forging operation so that the processing route can be optimised. The two dimensional finite element analysis described in reference one has been used in this work to model a number of commercial forgings in a range of materials.

The main limitation that restricts the application of finite element techniques to forging simulation is a lack of basic understanding of both the specific material flow behaviour and the lubrication conditions. Thus before any modelling work can be undertaken an extensive testing program has to be carried out so that a valid constitutive relationship for the material together with the appropriate lubrication conditions can be defined. Clearly it is essential that the material used for this work is representative of the forging billet stock and that the latter is highly consistent.

The material data used in this work was obtained from small scale pieces forged in a computer controlled 100 tonne isothermal press at constant strain rates, between  $10^{-4}$  and  $3 \times 10^{-2} \text{ s}^{-1}$ , for a range of strains, 0 to 1.5, and temperatures, typically over a  $200^\circ\text{C}$  range. The lubrication conditions were assessed from Cockcroft ring tests. Adequate representation of the material behaviour of a number of alloys has been obtained which includes the nickel based alloys Nimonic alloy AP1, Inconel alloy 718, Udimet 720 and Waspaloy and the titanium alloys IMI834 and IMI318. Typically the flow behaviour can be predicted to within  $\pm 5\%$  of the experimental data.

The model has been used to predict the loads obtained on the 3200 tonne isothermal press installed at Doncasters Monk Bridge Limited. Good agreement was obtained with the press loads being within  $10\%$  of the predictions. The specific constitutive relationship used is capable of indicating the microstructural development within forgings and results will be presented which illustrate the good correlation obtained between the predicted and actual microstructures obtained.

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See programme, page 18.

Isothermal Forging: Forming close to final shape  
with demanding materials and complex geometries

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Isothermal forging is a relatively recent development for the production of shapes close to final geometry. As the dies are continuously maintained at forging temperature, the good formability of the materials can be controlled throughout the entire forming operation. Hence, the material can flow into narrow clearances of the die yielding forgings with very complex shapes. This is particularly true if materials with superplastic properties are involved.

It is obvious that from the new net shape process, savings on operations and material are to be expected. The process also promises more design freedom and improved properties concerning integrity and homogeneity. On the other hand, higher machine and die cost as well as longer processing times have to be considered as compared to conventional forging. Therefore, when choosing applications, the economical issue has to be carefully assessed.

The paper starts with the fundamentals of the process, covering materials properties, particularly superplasticity. Materials involved are mainly titanium alloys for medical implants, but aluminium and copper alloys as well as Ultra High Carbon steels for machine parts are also considered. Technical aspects of series production on a 800-t-capacity press are then discussed. Finally, economical analysis is demonstrated on some real components.

See programme, page 18.

Application of Recrystallization Behaviour in  
Quantification of Deformation

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7 Figures.

The search for the origin of certain product deficiencies resulting from certain forming processes and thus, the desire to improve on product quality, has long provided stimulation for studying the details of metal flow. From a particular forming practice, estimates of the amount of plastic deformation or its distributions within the workpiece, could be useful as a basis for assessing the behaviour of the latter, and in identifying the severity of deformation producing satisfactory properties.

Many analytical methods that have been developed in attempts to provide this information, only give results that are primarily concerned with calculation of working loads, and to a lesser extent with overall flow, rather than with the detailed distributions of stress and strain. The individual solutions are time consuming, and detailed material properties cannot be included directly in the theoretical solutions. Questions therefore remain with regard to the accuracy of the solutions and the efficiency of the computations.

This paper illustrates the application of recrystallization behaviour in evaluating deformation in working processes. Since recrystallized grain size is a function of the amount of prior deformation applicable to all metals and alloys that could be deformed appreciably, and which are being used in forming processes, the technique can be used with reliability, as a means of quantifying deformation.

See programme, page 18.

Mandrelless Rotary Forging : Theoretical Modelling and Experiments

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Rotary forging is a well established industrial process, whereby cylindrical workpieces are brought to near net shape by a large number of short stroke and high speed pressing operations carried out in a set of radially aligned reciprocating dies, into which they are fed by one or two rotating chuck heads. In order to avoid twisting, motions are synchronised, so that deformation can only take place when the chuck heads have been momentarily stopped. Final shape is then achieved by a succession of workpiece forging passes and rotations.

The process can be used to manufacture hollow tubes of variable outer diameter, the interior surface of which is carefully controlled, with an aim at constant strength geometry. This can sometimes be achieved by making use of shaped mandrells, but there are many instances where it is not possible to do so, e.g. when the ends of the tube are thinner than its central portion and in some hot forging situations, due to thermal contraction problems. As geometry evolutions strongly depend on the material's properties and response to deformation (possible strain hardening or softening through dynamic recovery and/or recrystallisation), tool geometry, tool-workpiece interactions, and selected work conditions (temperature, feed speed, ...), the optimum procedure very often derives from costly trials and errors, associated with careful dimensional measurements.

The paper describes an original finite differences model which takes most of the experimental parameters mentioned above into proper account, and makes it possible to predict the stress field in the forged tube, along with its dimensional evolution (length and wall thickness). The model is based on straightforward assumptions as regards hammer die geometry, through-thickness stress distribution, outer diameter-wall thickness relationship, and tool-workpiece interface friction condition. Major stress components are approximated from the mechanical equilibrium conditions of volume elements, whereas local metal flow  $\underline{D}$ , is derived from the combination of two motions, one of purely radial contraction, and the other of tangential elongation, in such a way as to satisfy the constant volume condition ( $\text{div} \underline{D} = 0$ ).

Total work  $W$  can then be computed, while taking deformation and friction components into account over the whole deformed tube volume. Minimising  $W$  eventually leads to estimate profile index  $a$ , which gives access to overall dimensional evolutions. The model sheds some theoretical light on the sometimes limited range of practical work conditions (die refusal or draw-in situations).

The paper also reports on validation tests carried out on aluminium thin wall tubes submitted to four-stroke rotary forging : theoretical and experimental dimensional evolutions appear to be in very satisfactory agreement.

See programme, page 18.

Squeeze Forging - a near net shape technique  
for high strength applications

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The squeeze forming or squeeze forging process is a manufacturing technology combining the principles of both, casting and forging. Due to the applied pressure during the solidification of the melt, casting defects are avoided. The pressure feeds liquid metal into shrinkage cavities and encourages a particularly faithful reproduction of a detailed die surface. In other casting processes an air gap often forms at the mould/metal interface. This is suppressed by the pressure which is maintained throughout and beyond crystallization. The cooling rate is therefore much higher than in other casting processes and produces fine grained structures with small dendrite grain sizes.

In contrast to other developments in squeeze forming, a main point of research in this approach lies in the plastic deformation of the ingot after primary shaping. After pouring the liquid metal into the die cavity and the pressurized solidification a forging operation takes place. The plastic deformation changes the casting's microstructure into a typical forging texture and, therefore, a substantial improvement in strength and plasticity is expected.

This paper describes the basic processing procedure and processing parameters of squeeze forging. A general view is presented on the material properties and the microstructure obtained in first squeeze forging experiments. Until now, aluminum alloys have been used, but an expansion to other metals, possibly steel and composite materials, is intended.



See programme, page 18.

# HIGH TEMPERATURE PROPERTIES OF DIE MATERIALS FOR ISOTHERMAL FORGING

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To clarify the characteristics of various materials which will be able to use as isothermal forging dies, quantitative measurements and forging tests are performed. According to the die temperature of isothermal forging, 1173K for titanium alloy and 1323K for nickel-base superalloy, tests are done mainly in high temperature range. Testing materials selected are two superalloys, IN-100 and TRW-NASA-VIA, three refractory metals, TZM, TZC, and W-2ThO<sub>2</sub> and three ceramics, SiC, Si<sub>3</sub>N<sub>4</sub>, and SIALON. Hardness, thermal expansion and tensile strength data, that it is important to use the material as isothermal forging dies, are measured and isothermal forging test of nickel-base superalloy Mod.IN-100 as workpiece is made. As a result, quantitative data on high temperature of materials useful for designing the isothermal forging dies could be obtained. And the forging test data with respect to actual use suggest that forging with ceramic dies in air is more convenient than with refractory metal dies in inert gas.

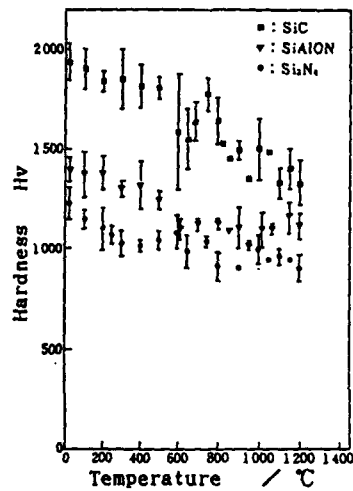


Fig.1 Effect of temperature on hardness of ceramics

Table 1 Isothermal forging properties using various die materials

	Atmo- sphere	Die material	Die strength $\sigma_{0.2}$	Die filling	Oxidation of die	Oxidation of backers	Removability of lubricant	Chamber
A	Ar	TZM	410MPa 1050 °C	○	○	○	○	Need
B	Vacuum	TZM	410MPa 1050 °C	○	○	○	○	Need
C		W-2ThO <sub>2</sub>	450MPa 1050 °C	○	○	○	○	Need
D	Air	IN-100	245MPa 1050 °C	○	△	×	×	No
E		SIALON	3200MPa(c) 830MPa(b) RT	○	○	×	○	No

c:Compressive strength, b:Bending strength, RT:Room temperature, Good: ○ → △ → × :Poor

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#### LARGE FORGINGS FOR NUCLEAR POWER GENERATING EQUIPMENT

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Forgings intended for nuclear power stations both by their size and by their extreme demands imposed on their quality rank among the most exacting of products. Forged pressure vessel rings are improved by piercing the blanks with a hollow mandrel to remove the defects common in the core material. Vessel rings are also being turned out with pre-forging pipe stubs or, which is even more advantageous, with stubs formed by lateral drawing.

Forged plates are another demanding product. To avoid the need to weld together heavy rolled plates, such plates up to 5 m in diameter are now being forged directly, and larger diameters are produced by developing the shells of forged tubes.

Pressure vessel bottoms are produced by pressing from rolled or forged plates, and their pipe stubs are formed by pre-forging or drawing.

See programme, page 19.

## **Microstructural Engineering of Near-Net Shape Casting**

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Conductive and convective heat and mass transport and other macroscopic engineering phenomena are the processes that determine how microstructure forms during materials processing. The mechanisms involved must be thoroughly understood if the microstructures of manufactured components are to be engineered to withstand the stringent service demands made upon them by modern design methods. This paper reviews current understanding of the macroscopic processes that determine how alloy microstructure forms during near-net shape casting, that is casting in moulds shaped so as to produce a cast component virtually identical to the final engineering component. Engineering components produced in this way obviously do not undergo major mechanical deformation so that the structure and properties of the final component are determined almost entirely by the micro- and macro-structures that form as the alloy solidifies.

The paper will review the theories of alloy solidification and of heat removal into permanent shaped moulds. The control that can be exerted in an engineering environment over the phenomena - interface velocity, local cooling rate, temperature gradient etc - that control the morphology of the solidification interface as well as microstructural features such as interdendritic spacing and cell size will be assessed.

Microsegregation processes will be outlined and an analysis presented to show how solid and liquid diffusion processes influence microsegregation. Equations will be developed from which non-equilibrium solidus temperatures can be predicted together with the extent of micro-segregation, both of alloying elements and of deleterious impurities including dissolved gases. The role of natural convection processes within the interdendritic zone will then be considered and the strength and permanency of natural convection currents assessed, both within the free liquid and within the interdendritic zone. The role that natural convection plays in determining macrostructure will then be considered, particular attention being paid to the transition for columnar structure to equiaxed structure.

Flow behaviour of, and within, partially solidified alloy structures will then be considered and the changes that can be made to the microstructure of engineering components through control of such flow will be outlined. Processes utilising the thixotropic behaviour of partially solidified alloys and the effects of vibration will thus be reviewed. Finally, the control that can be exerted over the formation of feeding porosity and gas porosity will be discussed and methods outlined of correcting for the deleterious effects of porosity.

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See programme, page 19.

Light metal investment casting

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Investment castings acc. to the lost wax process in the light metals Aluminium, Titanium and Magnesium are widely used within high-tech products of aircraft- and aerospace industries, electronics, optics and medical technology.

By means of numerous examples of castings there will be shown possible aspects for economical and cost saving solutions for an idea in a product. The possibilities of designs for casting materials are nearly unlimited for investment castings. The designer has the possibility to achieve the requirements in contours the consumer is asking for nearly without further machining and joining.

It will be reported about mechanical properties of cast high temperature Titanium alloys as well as first results of cast test samples of intermetallic phases.

See programme, page 19.

FORMATION OF SOLIDIFICATION STRUCTURE IN  
A TWIN-ROLL RAPID SOLIDIFICATION PROCESS

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The twin-roll casting to produce thin metallic strip directly from the molten state has merits of near net shaping and rapid solidification. In this process, it is very important to control the strip thickness and get better surface and internal quality of strip. In this study, the experiment to produce rapidly solidified strip was carried out by using a laboratory-scale twin-roll caster. On the basis of the experimental results, factors affecting the strip thickness, surface quality and solidification structure of strip were examined. Furthermore, the interrelationship between the formation of solidification structure, growth of solidified shells and the heat transfer in the process was investigated.

In the experiment, austenitic stainless steel (SUS304, melting weight 5-8kg) was cast to thin strip. Main operational parameters in this experiment are roll surface velocity, contact arc length between roll and molten metal and roll supporting force. The roll surface velocity and the contact arc length were changed in ranges of 0.07-2.36m/s and about 30-85mm, respectively.

As the result of the experiment, the cast strip of 0.5-3mm in thickness and 100mm in width was obtained. It has been possible to cast the thin strip with good surface and internal qualities. The contact time between roll and metal is the most important factor to control the strip thickness under low roll supporting force.

Regarding the solidification structure of the cast strip, two kinds of the structure were observed; one has both the dendritic and equiaxed zones, the other only the dendritic zone. The ratio of the equiaxed zone to strip thickness increases with increasing roll surface velocity. By comparing the observed solidification shell thickness (namely, thickness of the dendritic structure) with the shell thickness at the roll nip estimated by using a heat transfer model, the overall heat transfer coefficient between roll and metal has been found to increase with increasing roll surface velocity. Thus, the formation of the solidification structure is affected by the heat transfer resistance between roll and metal and the sudden change in cooling rate before and after leaving the rolls.

See programme, page 19.

Metal Injection Molding - Microstructural  
Design by enhanced sintering techniques

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Among powder metallurgical near net shape processes metal injection molding is one of the most promising techniques for mass-production of small and complex shaped structural parts. For injection molding fine particle metal powders are mixed with a sufficient amount of organic binder, which has to be removed after the shaping process.

In contrast to conventional powder metallurgy injection molded parts are extremely porous after debinding (30 - 50 % porosity). Due to the viscous flow of the particles embedded in the organic binder during the injection molding process the particles do not undergo a remarkable plastic deformation. Hence, injection molded and dewaxed parts consist of homogeneously arranged, undeformed fine powder particles and for densification of injection molded and dewaxed green parts up to nearly full density enhanced sintering techniques e.g. rate controlled sintering should be chosen. By applying materials-specific sintering programs it is possible to achieve the desired mechanical, physical or chemical profile of properties for injection molded structural parts.

In the present paper results of materials development for the injection molding process are presented. High efficiency of e.g. soft magnetic or corrosion resistant materials is discussed. Well-aimed microstructural development is demonstrated by mechanical, physical and chemical properties of different injection molded materials.

See programme, page 20.

Short Fibre Reinforced Magnesium Alloys

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Magnesium alloys have assumed increased importance as construction material where weight and hence energy must be saved. The disadvantages of low strength, low elastic modulus, poor fatigue resistance and insufficient high temperature strength prevent their use in applications where strict requirements must be met.

Fibre reinforcement can remove many of the disadvantages and enable alloys to meet many demands in aircraft, space and automobile applications.

The production techniques and properties of short fibre reinforced magnesium alloys produced by powder metallurgical techniques and squeeze infiltration are discussed. Many problems arise in the production of fibre reinforced alloys by powder metallurgical methods. Fibre damage and inhomogenous distribution necessitate appropriate production techniques. The advantage of the squeeze infiltration process lies in its universal applicability as well as in the possibility of graduated or partial component reinforcement. In this work the structure, mechanical properties, wear resistance and thermal expansion of short fibre reinforced magnesium alloys (saffil fibre) produced by P/M methods and squeeze infiltration are discussed.

See programme, page 20.

#### DIRECTIONALLY SOLIDIFIED Al-Ni(Me) EUTECTICS

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The directional solidification of fibrous eutectical materials is a useful method for production of anisotropic structural materials with extraordinary properties. The uniform structure develops as a sum of two transport processes along (i) and perpendicularly (ii) of the liquid - solid phase boundary. The regular directed structure can be built by balancing the alloy concentration, the temperature gradient and growth velocity.

Crystallisation experiments of Al-Al<sub>3</sub>Ni eutectics were made to study the effects of 0,1-0,5 % Cu, the thermal and gravity parameters on the structure. It was experienced that the planar crystallization front changes onto convex surface on influence of increasing growth velocity, copper content or gravity. Besides the fibrous eutectic a degenerated coarse eutectic also appears. Along the sample a macrosegregation is also observed and measured. The structure characteristics were determined by quantitative metallographic methods.



See programme, page 20.

Advanced Melting Techniques for Superalloys

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The last twenty years have seen the arrival of vacuum induction melting, coupled with vacuum arc remelting and electroslag refining, together with metal powder technology improving the properties of all the existing alloys and forms. These processes have been developed and optimised over the last few years so that the product quality and consistency now being produced is near to theoretical limits. There are, however, continuing demands for further improvements in quality, particularly cleanness, which is likely to have very significant effects on mechanical properties and the life of critical components in aero gas turbines.

Further major improvements in cleanness are unlikely unless alloys can be melted in refractory-less systems such as Plasma Arc Melting and Electron Beam Cold Hearth Melting and Refining. This paper proposes to give an alloy producers perspective of these techniques from a technical and commercial viewpoint.

See programme, page 20.

## CASTABILITY TEST : MODELLING AND RELATED EXPERIMENTS

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Castability tests, also named fluidity tests, are a class of cast-house tests in which hot metal is caused to flow in a long channel of small cross section. The length the metal flows before it is stopped by solidification is a measure of its fluidity, or castability /1/. From the technical point of view, its value can be used to forecast possible difficulties to fill thin parts of the casting.

Technical and scientific literature on the subject mentions several parameters. Besides the geometry of the test sample and the thermal characteristics of the metal and of the mould, a major importance is given to the solidification interval of the alloy, in relation to the more or less dendritic morphology of the solidification front.

The castability length is strongly dependent on hydrodynamic parameters, typically the flow velocity expressed in terms of a Reynolds number. In a series of experiments on Al-Cu alloys, PRATES and BILONI /2/ showed that the grain structure changes from columnar to mainly equiaxed, in correlation to the change in flow regime from laminar to turbulent. PAI and JONES /3/ observed similar changes of structure on tin alloys. They discussed it with reference to the mould-metal thermal exchange.

The goal of the present paper is to study the influence of hydrodynamic parameter on the solidification structure. An experimental device was built for measuring the castability length for metal injected in a quartz tube. The velocity is measured by using a video-recorder and viewing the injection test image by image. The results are discussed by using theoretical models for heat flow and formation of the solidification structure.

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See programme, page 20.

#### THE MICROSTRUCTURE OF THIXOTROPIC ALLOY SLURRIES

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A number of alloys based on aluminium cobalt and iron have been partially melted to a given fraction liquid in an isothermal environment and subsequently quenched to allow the investigation of microstructural changes in the slurry with time. These alloys have also been given different preparation treatments prior to partial melting to determine their effect on the slurry microstructure. Finally tests have been carried out to establish the relationship between the flow behaviour of slurries and their structure.

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#### MICROSTRUCTURAL DEVELOPMENTS IN POWDER METALLURGY

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The evolution of disc materials follows closely that of the turboengine performances : the latter justifies and is partly determined by the former. Powder metallurgy was introduced for the making of the discs of the modern aeroengines to process parts with well controlled macro-segregation free materials allowing the obtention of homogeneous fine grain microstructures having an excellent resistance to Low Cycle Fatigue. It will be seen that the more recently introduced requirements for damage tolerance together with the increase in operating temperatures is shifting the locus the microstructural optimization, putting new constraints on alloy design, and leading to reconsider processing routes.

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POWDER METALLURGY PREFORM DESIGN FOR POWDER  
FORGING: A PHYSICAL SIMULATION METHOD USING A  
MODEL MATERIAL.

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To produce light weight aluminium powder metallurgy parts two steps are required. First, a preform is obtained by cold uniaxial pressing (relative density far 0.80). Net shape forging is then performed on a conventional forging press after heating up the preform at high temperature. The main problem is to find the best preform geometry. Two main conditions must be verified for the final shape: the first one is a net shape part with a density equal to one. The second one is a sufficient plastic deformation of the powder particles in order to break up the oxide layers present at particle surfaces that hinder tough interparticle contact.

Preform optimization to achieve these goals can be long and expensive if trials and errors technique is used by processing real metal powder parts. So we develop an alternative economic laboratory design procedure using a model material, that is plasticine balls. The experimental techniques for producing plasticine balls and processing of billets or preforms are described. The rheological properties of this plasticine is determined and is compared to that of P.M. aluminium powder. Practical cases of preform design are presented.

Interest of this technique is discussed by comparison with the computer simulation of powder processing by Finite Elements Methods.

See programme, page 21.

# MICROSTRUCTURAL FEATURES OF THE EXTRUDED Al-20Si-3Cu-1Mg ALLOY PREPARED FROM RAPIDLY SOLIDIFIED POWDER

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Si-dispersed Al alloys prepared from rapidly solidified powders appear to be a very important Al alloy class, used for engine and compressor parts in automobile, aircraft and electric industries, thanks to their excellent wear resistance, good thermal stability and low thermal expansion coefficient. Consolidation of the atomized powders by hot extrusion is a crucial processing step, through which required properties are achieved. The properties of the alloys are largely determined by the as-extruded microstructure. An analysis of microstructure for a representative Si-dispersed Al alloy, Al-20Si-3Cu-1Mg in the as-extruded state, has therefore been conducted using optical and electron microscopy. Dispersed Si crystals in the Al matrix are a main constituent phase, the size and distribution of which are of significance for final properties. It is found that block-like Si-crystal particles are redistributed during extrusion, being aligned in the direction of extrusion. Massive fine granular Si-crystal particles are sensitive to extrusion temperature. Particular at above 400°C, they show a tendency of coalescence. The reciprocal size of Si-crystal particles has been found to be proportional to logarithmic temperature-compensated strain rate. It is thus suggested that the Si-crystal size can be regarded as a representative structure feature for the control of extrusion temperature. The Al matrix of the extruded material is micro-inhomogeneous. It is generally composed of grain, subgrains and microcells, exhibiting a recovered appearance. A significant number of microcells are a main structural feature of the extrudate. Since the massive Si-crystals are dispersed in the matrix and prior powder particles, although greatly deformed, are retained in the extrudate, motion of dislocations is difficult. It is thus thought that the micro-cells are formed from high-density dislocation tangles within subgrains during the air cooling subsequent to extrusion. Dynamic recovery is the deformation mechanism of the alloy during hot extrusion. Static recrystallization during the cooling is generally inhibited by small granular particles, although a few subgrains are decomposed where there are no particles pinning.

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Effect of the consolidation method on the microstructure of  
PM/RS aluminium alloys

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The methods of rapid solidification enable the production of aluminium alloys with finer microstructure than conventional ingot metallurgy. However, the improved properties gained by refining the microstructure with rapid solidification may be lost to a certain extent during the consolidation process, e.g. due to thermal coarsening of the microstructure.

Possibilities of refining the microstructure for example by varying the alloy composition or by minimizing coarsening during the compaction of these powders will be discussed. In order to reduce the coarsening rate of the microstructure during compaction, the powder has to be consolidated at the lowest possible temperature. Therefore, the effect of the consolidation process on the preservation of the fine microstructure is investigated for three different consolidation techniques,

- a) extrusion
- b) high energy rate forming (Dynamapack)
- c) swaging

The investigations by optical metallography and transmission electron microscopy of aluminium-based powders and their extrusions showed, that the microstructure of the three methods are very different. The finest microstructure was found in the swaged material. This effect is due to the comparatively low process temperature adequate for this consolidation method. The results of the investigations will show the importance of an optimised temperature control during consolidation.

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**STUDY OF PLASMA-SPRAYED GRADED W-CU COMPOSITES USING GLOW DISCHARGE SPECTROMETRY COMPARED TO QUANTITATIVE IMAGE AND ELECTRON PROBE ANALYSES**

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Powder routes, especially those involving plasma spraying, is highly suitable for achieving "near-net" shape and/or composite materials. Novel graded W-Cu composite layers 1 mm thick exhibiting a continuous evolution from quasi pure tungsten to pure copper was thus obtained.

This type of material is basically heterogeneous on a variety of scales : that of the particles, that of the elementary layers of co-deposited W and Cu powders (corresponding to one or a few torch passes) and that of the total composite layer. Consequently, the study of such materials required the development of new analytical methods or at least new combinations of methods, to investigate the microstructure-process-properties relationship.

Glow Discharge Spectrometry (GDS), conventionally used for coating and surface analyses, was developed to be applied to these composites. It has been demonstrated that the method was unique in giving a continuous analysis of the material as a function of the depth which in addition was integrated over a fairly large area (of a few mm<sup>2</sup>). GDS was applied to a 1 mm thick graded composite and validated by X-ray fluorescence analyses of the bottom of the GDS crater at various depths (figure 1). The chemical contents vs. GDS signal were given by abacuses resulted from previous GDS carried out on thick homogeneous samples the composition of which had been accurately determined using inductively coupled plasma (I.C.P.) technique.

These same homogeneous materials were studied using quantitative image analysis (Q.I.A.) the results of which showed a discrepancy, especially for high W contents, with those given by electron probe micro-analysis (E.P.M.A.) and conventional helium pycnometry or weight/volume method (figure 2). This was discussed in terms of experimental conditions and intrinsic factors linked with the composite material.

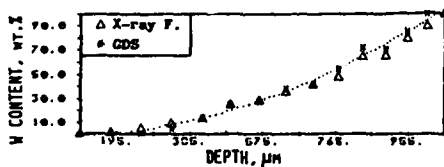


Fig.1 : W depth profile in the graded composite given by GDS and X-ray fluorescence.

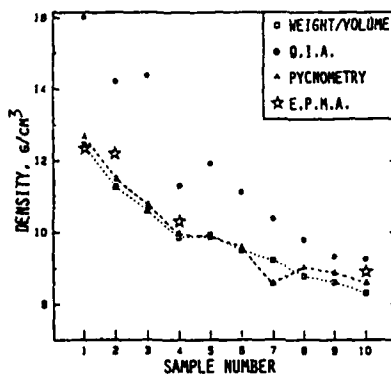


Fig.2 : Density of a series of samples exhibiting various W contents.



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SPRAY DEPOSITION OF HIGH PERFORMANCE  
ALUMINIUM ALLOYS VIA THE OSPREY PROCESS

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The Osprey spray deposition technology is a rapid solidification process capable of producing dense preforms of different shapes in one integrated operation. Compared to conventional ingot casting this offers significant metallurgical advantages by extending the range of composition beyond that normally possible without rapid solidification. In addition, compared to powder metallurgy, considerable economic benefits can be obtained by reducing the multiple steps between atomisation of the metal and compaction of the preform of the PM route to simply one operation.

Fundamental research at Osprey Metals, patent holder and developer of this technology, and other material and production orientated activities have brought this technology to industrial maturity. As a result, the main emphasis is shifting from process optimisation to alloy development and the search for suitable application of these high performance materials.

Using examples of the alloy systems AlSiCu, AlZn, AlCu and metal matrix composites in comparison with conventional and PM alloys, the potential and the special characteristics of these materials will be demonstrated.

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## DEVELOPMENT OF HIGH SPEED STEELS PRODUCED BY THE OSPREY PROCESS

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Although high speed steels (HSS) are now widely employed in a variety of wear and cold forming applications, their major use is still for metal cutting tools where a fine uniform dispersion of carbides is required for good performance. Conventional wrought high speed steel suffers from severe segregation and a non-uniform distribution of carbide particles, resulting in poor in service properties. The process of powder metallurgy allows the manufacture of high speed steel parts with reduced segregation and a homogeneous dispersion of carbides. However, there are several problems involved in the process. In the case of compaction and sintering route, a strict temperature control (e.g. within  $\pm 2^\circ\text{C}$  for M2 HSS), which is not easy to achieve in most industrial furnaces, is essential in order to develop the appropriate microstructure for optimum mechanical properties. The use of hot consolidation methods is restricted by the relatively high costs involved. A technique which offers the potential for manufacturing full density homogeneous material with a reduced processing cost is therefore attractive. In this case the Osprey process involving the continuous spraying of partially molten metal onto a substrate meets this objective. In this paper we will report and describe the results of an investigation on the properties and heat treatment response of M2, ASP23 and T15 HSS produced by the Osprey process. The results will be compared with those of materials produced by conventional and powder metallurgy methods.

See programme, page 22.

THE OSPREY PROCESS - A VERSATILE MANUFACTURING TECHNOLOGY FOR THE  
PRODUCTION OF SOLID AND HOLLOW ROUNDS AND CLAD (COMPOUND) BILLETS

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Equipment for the manufacture of spray-deposited, rapidly solidified, thick-walled tubes directly from molten alloy is described. Examples are given of roll sleeves in high carbon, high speed steels. The superior microstructure of the spray-deposited alloy is shown to result in a longer life in service compared to conventionally produced rolls.

The manufacture of spray-deposited billets in a horizontal mode is also described with examples given of high speed steel billets. Again superior properties are evident compared to conventionally produced high speed steel as a consequence of the finer microstructures generated and the absence of macro-segregation.

The versatility of the Osprey Process is illustrated by its application to clad or compound tubes or billets where combinations of different materials can be economically produced, offering a unique opportunity for tailor designed products to suit many individual applications. Examples are given of stainless steel/low alloy steel compound bar. The stainless steel is shown to exhibit properties similar to more expensive ESR material.

To conclude, the economic benefits are demonstrated by comparing the number of process operations required by the Osprey Process with typical ingot and P/M routes for the manufacture of high speed steel billets.

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See programme, page 22.

## IN-FLIGHT PHENOMENA DURING VACUUM PLASMA CO-SPRAYING OF TITANIUM-BASED COMPOSITES

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In principle, titanium-based composites offer an attractive combination of properties, including high strength, low density and good resistance to corrosion. Of the processing techniques available, the vacuum plasma spray (VPS) process appears attractive in several respects. Melt containment, and possible contamination from crucible contact, are eliminated, and both high melting point and oxygen-sensitive materials can be handled. Composite deposits can be produced by co-spraying. For example, titanium and ceramic powders can be fed into a gas stream, which is heated and accelerated by a DC plasma. Typically, flight times of a few ms and velocities of a few hundred  $\text{m s}^{-1}$  precede impact of the particles onto a substrate. The ceramic particles may melt in flight or may become incorporated into the deposit by impact with metal droplets or other mechanisms. This allows the production of Ti-MMCs of good general soundness, with impurity levels dictated primarily by the quality of the powder stock used. However, several aspects of the processing require optimization before high microstructural integrity and homogeneity can be obtained in as-sprayed composites produced in this way.

In an attempt to optimise the spraying conditions, a test has been devised to characterize the spatial distribution of droplet sizes within the spray cone, as an aid to modelling the frequency and nature of in-flight collisions and post-impact spreading behaviour. These studies indicate that in-flight collisions are relatively rare events, but that droplet superheat and impact velocity are important in controlling porosity levels. Additional observations, using high speed photography, have revealed the presence of large amplitude pulsations in plasma plume dimensions (particularly in the spraying direction), with an irregular period of the order of a few ms. The microstructural changes taking place during the spheroidisation process are being studied.

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THE SUPERALLOYS: CURRENT STATUS AND FUTURE PROSPECTS

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It is generally agreed that after about fifty years of continuous improvement during which the maximum operating temperature of superalloy components has been raised by something like 400 °C, these alloys have now probably reached the limit of development. However no really attractive replacement material has yet emerged to meet the demanding requirements of load-carrying capacity and temperature capability for critical components such as high pressure turbine parts.

Accordingly it appears that further advances in engine performance will depend at least in the short-term, on more efficient usage of existing materials.

In the paper selected examples will be given to demonstrate the progress that has been made in improving the performance of superalloys and to indicate the potential for further enhancement in critical areas of usage. Recent work on improved coating techniques to improve resistance to environmental attack will be mentioned.

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## High Temperature Creep and Microstructure of the Monocrystalline Nickel-Base Superalloy SRR 99

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Samples of the monocrystalline nickel-base superalloy SRR 99 were creep-deformed in the temperature range of  $750^{\circ}\text{C} \leq T \leq 1050^{\circ}\text{C}$  at constant stresses  $\sigma$  between 150 MPa and 750 MPa. In this abstract, reference will only be made to creep tests conducted at  $900^{\circ}\text{C}$ . Similar tests at lower and higher temperatures are under way and will be reported at the conference.

Independent of the applied stress, all creep curves exhibit similar stages, when plotted in the  $\log \dot{\epsilon} - \epsilon$  diagram ( $\epsilon$ : strain,  $\dot{\epsilon}$ : strain rate): primary transient creep – a range of minimum creep rate  $\dot{\epsilon}_{\min}$  – "steady state" creep – tertiary creep leading to fracture. Special attention was devoted to the study of the transition from the initially cuboidal  $\gamma'$ -particles to the so-called  $\gamma/\gamma'$ -raft structure in relation to the details of the creep curve and the dependence on the magnitude of the applied stress  $\sigma$ .

The identical shapes of the creep curves for different particle structures indicate that creep is controlled by a deformation mechanism which is independent of the prevailing  $\gamma'$ -particle morphology (cubes or rafts). This conclusion is also based on the results of studies on "pre-raftered" specimens. In all cases investigated so far, pre-raftered specimens exhibited inferior creep properties.

Detailed mechanical tests were performed on specimens containing different  $\gamma/\gamma'$ -morphologies in order to determine the stress exponent  $n$  and the threshold stress  $\sigma_0$  in the relations  $\dot{\epsilon} \propto \sigma^n$  and  $\dot{\epsilon} \propto (\sigma - \sigma_0)^{n_0}$  respectively, where  $n_0$  is the stress exponent of the particle-free matrix.

The results of the microstructural studies (scanning and transmission electron microscopy, X-ray Berg-Barrett topography) will be discussed in conjunction with the data obtained in the mechanical tests.

See programme, page 23.

THE ANISOTROPY OF MECHANICAL BEHAVIOUR IN NICKEL BASED  
SINGLE CRYSTAL SUPERALLOYS FOR TURBINE BLADES

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The nickel based single crystal superalloys are presently being used as vanes and blades in some advanced gas turbine engines. The development of constitutive models for such anisotropic materials requires the characterization of the mechanical behaviour along various crystallographic orientations. The effects of orientation, microstructure and temperature on the tensile, creep and low cycle fatigue behaviours of several representative single crystal superalloys have therefore been evaluated.

The superalloy CMSX-2 was tested in tension along the [001], [111] and [011] axes, between room temperature and 950°C. At room temperature, the [111] oriented single crystals exhibit the highest yield strength, whereas they are the weakest at 760 and 950°C. At all temperatures, the [001] single crystals are stronger than the [011] ones, and they both deform by octahedral slip. However, the Schmid's law is not obeyed at 650 and 760°C, where the CRSS for octahedral slip is higher for the [001] orientation than for the [011] one. In the near [111] oriented single crystals, primary cube slip is operative from room temperature to 950°C.

The anisotropic creep behaviour of several high strength single crystal superalloys was investigated between 760 and 1050°C. It is shown that the modification of the microstructure, characterized by the change of the  $\gamma'$  particle size, produces dramatic effects on the creep behaviour at intermediate temperatures (760-850°C). As an example, the creep strength at 760°C and 750 MPa of CMSX-2 single crystals containing  $\gamma'$  precipitates of 0.5  $\mu\text{m}$  is optimum for a near [001] stress axis (stress-rupture life of about 1000 hours), while it is catastrophically poor near [111] (stress-rupture life of only 20 to 30 hours). However, for the same creep conditions, CMSX-2 single crystals containing finer precipitates, i.e. 0.2  $\mu\text{m}$ , exhibit the highest creep strength near [111] (stress-rupture life more than 1000 hours), whereas the stress rupture life of [001] single crystals is reduced by a factor of two. At higher temperatures (950-1050°C), the effects of orientation and microstructure on the creep behaviour of single crystal superalloys are strongly reduced. The results of this study have clearly established that the general conclusions drawn from the creep behaviour of the CMSX-2 alloy can be extended to other high  $\gamma'$  volume fraction containing superalloys (PWA 1480, CMSX-4, MXON).

Strain-controlled low cycle fatigue tests were run at 650 and 950°C on single crystals of the AM1 superalloy, with various orientations. This alloy has been selected by SNECMA for the M88 advanced military engine. For a given total strain range, the fatigue life follows the pattern : [001] > [011] > [123] > [111]. When presented on a total stress-range vs. cycles to rupture basis, all experimental data lie on a single straight line, which shows that the effect of orientation is essentially due to the strong anisotropy of the Young's modulus of the single crystals.

See programme, page 23.

PHASCALC: An Improved Computer Programme for the  
Calculation of Phasekinetics, Microstructural Parameters  
and Microstructural Instabilities in Nickel-base Superalloys

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In the seventies computer-programmes, like Phascomp, has been developed in order to prove the microstructural sensitivity to  $\sigma$ -proning of a Master heat of nickel-base-superalloys. By the microstructural examinations (LiMi, SEM, TEM, electrochemical phase extraction and X-ray) of a series of vacuum investment casted and directional solidified specimens of Alloy 738 LC and IN 939, of a number of (Ni-Al-Cr-Ti-Ta-W)-based model alloys and the ODS-Alloys MA 6000, MA 760 now a broad basis exists to improve these former programmes. With a computer programme, which works on each type of IBM-PC's, the following features can be predicted:

- type, amount and chemical composition of the minor-phases: carbides, carbo-nitrides and borides;
- amount and chemical composition of  $\gamma'$ , including their solvus temperature and  $\gamma'/\gamma$ -mismatch;
- the composition of the residual matrix, their  $N_V$ - and  $M_d$ -values;
- the solidus and liquidus temperature range during solidification.

The calculation is based on experimental derived solubility factors, on accounting the activities by using mol-, respectively the atomic-percentages, a simplified Vegard's rules and by regression analysis. The report introduce in the principles and in the procedure of the programmes. For a certain number of alloys, the microstructural parameters are computed and compared with experimental results of x-ray examination of electrochemical phase extractions, by dilatometry and thermodynamical methods and with microstructural evaluations. The predicted microstructural features fit very well with the experimental obtained.



See programme, page 24.

On the configuration of superlattice dislocation pairs in the ordered  $L1_2$  structure.

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The unnormal temperature dependence of the yield behavior of  $L1_2$  phases has first been connected with the anisotropy of APB energies by Flinn (1960).

The mechanism now generally accepted is that of Kear and Wilsdorf (1962) which requires cross slip of the leading screw dislocation on  $\{001\}$  planes due to the anisotropy of the APB-energy.

The aim of this work was to find out whether the anisotropy of APB-energies or the elastic interaction between superdislocations determine the pair habit plane.

We analyzed dislocation pairs on the  $L1_2$   $\gamma'$ -phase of a single crystal Ni-based superalloy strained at 1253 K, a temperature where diffusion takes place.

Isotropic elastic theory was used in order to calculate the minimum of elastic interaction energy between the superdislocations of a pair as function of their character and habit plane orientation. Habit planes observed are compared with these results.

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## THE FINE STRUCTURES OF DISLOCATIONS AND THEIR MOBILITY IN ORDERED INTERMETALLIC ALLOYS

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Ordered alloys exhibit a variety of mechanical behaviours, from a flow stress that regularly decreases with temperature to the so-called flow stress anomaly or mixtures of both.

In a number of instances the anomalous behaviour is known to originate from properties that are intrinsic to dislocations (as opposed to interactions of these with extrinsic obstacles). The exact nature of dislocation cores has been the object of active controversy long after the flow stress anomaly had been characterized at a macroscopic scale. For instance, the mechanisms to explain the positive sensitivity of the flow stress to temperature remained founded on low resolution imaging of dislocations until the late 70s. It is only recently that TEM analyses of dislocations have become sufficiently documented because of the independent interest of different groups. There is now reasonable consistency between these groups on several areas while the interpretations may differ.

The  $L1_2$  structure (model alloy:  $Ni_3Al$ ) has by far received the largest attention both from a theoretical and an experimental point of view. A refined model for the flow stress anomaly was derived by Paidar, Pope and Vitek in 1982. It explains fairly closely the observed dependence of the flow stress upon the direction and the sense of the applied load. Under weak-beam TEM,  $Ni_3Al$  has shown to contain an unusually wide range of locking mechanisms. In fact, not only the classical Kear-Wilks configuration was proven to immobilize screw dislocations within a range temperature but specific dissociations of edge dislocations into Lomer-Cottrell locks were pointed out. Insofar as non conservative processes are concerned, the prediction made by Brown (1959) and Flinn (1960) that dislocations could dissociate by climb and that APBs could be dragged behind them has been verified. Surprisingly, there is some agreement within electron microscopists upon the fact that the deformation microstructures analyzed under dynamical as well as static conditions do not conform the mechanism of local pinning by core transformation of Paidar *et al.*

From samples observed after straining there is evidence that immobilized Kear-Wilks screw dislocations can undergo some motion by means of a kink mechanism toward regions where they can mutually annihilate. Kink motion is completely understood as long as one deals with Kear-Wilks configurations formed at low temperature. These are also present at higher temperatures but they tend to bend in their plane of dissociation (the cube plane) while the rest of the dislocation glides in an octahedral plane.

On the other hand, *in-situ* straining at temperatures reveals quite different information on the processes that are dynamically involved during deformation. Extensive dislocation motion is observed in cube planes, from very low to high temperature, and double cross-slip between cube and octahedral planes occurs in the domain of strength anomaly. Motion of screw superdislocations is jerky in both glide planes, attesting to the operation of a variant of the Peierls mechanism ("locking-unlocking"). Local stress measurements suggest the occurrence of a strength anomaly on the cube plane. The information derived from *in-situ* studies is thus inconsistent with the predictions of previous models. It is interpreted as the result of an increasing interaction between superdislocations and the lattice similar to that determined recently in beryllium.

While the work and the debate on  $L1_2$  alloys are presently very active, other systems are under investigation in order to complement our knowledge of dislocation mechanisms. This is the case of the  $L1_0$  and  $DO_{22}$  structures and more generally of the family of the titanium aluminides.

See programme, page 24.

INFLUENCE OF HEAT TREATMENT ON PHASE COMPOSITION  
AND FINE-SCALE FEATURES OF SOME NICKEL BASE SUPERALLOYS :  
A FIM ATOM-PROBE INVESTIGATION

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The relationship between the microchemistry of some nickel base superalloys and applied heat treatments have been studied with the help of a Field Ion Microscope combined with a time of flight atom-probe. The principle of these techniques is given elsewhere [1]. The atom-probe allows a microanalysis to be performed in a small region which can be easily located in field ion images. The mean spatial resolution is close to 2nm at the material surface while the depth resolution may attain a single atomic layer.

Two types of materials have been investigated, namely single crystal superalloys designed for turbine blades and polycrystalline materials prepared from prealloyed powders. Nickel base superalloys derive their excellent creep performance from the presence of a high volume fraction of ordered  $\gamma'$  precipitates (up to 70 %). As high temperature properties of superalloys are strongly dependent upon the lattice misfit, it is therefore of utmost importance to measure as well as to control the composition of both  $\gamma$  and  $\gamma'$  phases. The occurrence of local concentration gradients in the vicinity of phase boundaries is also of interest [2].

In this work, we will attempt to clarify the role of various precipitation sequences for a single crystal superalloy subjected to a double aging heat treatment. The influence of quenching on phase composition will also be discussed. The composition (as well as the volume fraction) of  $\gamma$  and  $\gamma'$  phase formed during cooling in solution treated materials will be compared to that of isothermally precipitated products.

The stacking fault energy is probably a major parameter which controls the solid solution strengthening in  $\gamma$  phase. It is clear that the occurrence of a short range order in the matrix will certainly influence this factor [2]. Because of its high spatial resolution, the atom-probe is a well suitable tool for studying the spatial distribution of addition elements in the solid solution. Microanalyses we made have shown that the role played by some solute elements [2] can be more subtle than just solid solution strengthening. Some short range fluctuations are for instance observed for Chromium with a spatial wave-length of a few nanometers.

**Acknowledgements** : This work has been made with the financial support of the Direction des Recherches et Etudes Techniques (DRET Contrat n° 87/031), in collaboration with the ONERA. Some of these researchs have been also conducted in connection with the LSG2M laboratory of Nancy within a national scientific program on single crystal superalloys.

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See programme, page 24.

CREEP RESISTANCE,  $\gamma'$  SHAPE CHANGES AND DISLOCATION STRUCTURES  
IN NICKEL BASE SINGLE CRYSTALS.

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High performance Nickel base superalloys for single crystal turbine blades such as CMSX-2 and AM1 have been developed during the last ten years in order to sustain the most difficult creep conditions.

Single crystals oriented near 10011 were grown and creep tested at 950°C and 1050°C under various stresses (120 to 200 MPa) both in tension and compression.

The initial microstructure is composed of a high volume fraction ( $\geq 65\%$ ) of cuboidal  $\gamma'$  precipitates 0.4 to 0.5  $\mu\text{m}$  in size obtained by an appropriate heat treatment. The  $\gamma$ - $\gamma'$  misfit parameter  $\delta$  for most of the recently developed alloys is of the order of  $-2$  to  $-3 \times 10^{-3}$  at about 1000°C.

Stress oriented coalescence of the  $\gamma'$  phase is of type N in these alloys with  $\delta < 0$ , i.e. one set of  $\gamma'$  plates normal to the applied stress tends to appear under tension tests and two orthogonal sets of plates parallel to the applied stress when tested under compression.

The  $\gamma'$  phase which is originally identified as the matrix since it surrounds the  $\gamma$  cuboids from all sides, thickens much more rapidly than the hardening phase  $\gamma'$ . Since it is actually the minority phase (only 35% in volume) it tends to become surrounded by the  $\gamma'$  phase as creep develops and the contiguity of the two phases is inversed:  $\gamma'$  becomes the matrix. Quantitative measurements of topologically meaningful parameters will be presented.

In the temperature range and stress range explored, the dislocations do not seem to split into partials and no stacking faults are observed. Most of the dislocations are located in the  $\gamma$ - $\gamma'$  interfaces and tend to lie close to a pure edge orientation thus forming high density dipolar walls on opposite sides of the matrix walls. By climb and glide these dipoles can annihilate at the edges of plates and would tend to disappear. They are constantly renewed by the glide of fresh screw dislocations bowing out between obstacles.

Static dislocation networks were observed under tension i.e. networks with Burgers vectors normal to the applied stress. Under compressive creep conditions on the contrary, active dislocation networks are densely knit in the cube oriented  $\gamma$ - $\gamma'$  interfaces parallel to the applied stress.

Both structures, despite their differences in morphology and in dislocation arrangements are able to exhibit a remarkable resistance to creep stresses.

See programme, page 24.

THE EFFECT OF THERMOMECHANICAL TREATMENTS ON SHORT-RANGE ORDERING  
AND CARBIDE PRECIPITATION IN A Ni-Cr BASED SUPERALLOY.

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The Ni-Cr based superalloy Nimonic 75 undergoes an order-disorder transformation, i.e. formation and dissolution of a short-range ordered  $\text{Ni}_2\text{Cr}$  phase, associated with significant variations of physical properties. This transformation can occur simultaneously with carbide precipitation and recrystallization and both latter phenomena can also affect the alloy properties. The main purpose of this study is to describe the development of short-range order (SRO) in Nimonic 75, identifying its impact on physical properties among the effects resulting from other simultaneously occurring microstructural alterations.

In this study various experimental techniques were adopted, i.e. electrical resistivity, hardness and differential calorimetry measurements, showing different sensitivity to different phenomena, with the aim to investigate the effect of thermal and mechanical treatments on ordering and precipitation kinetics. Hardness is particularly sensitive to the effects of coldwork and recrystallization, while resistivity and specific heat are considerably affected by ordering.

The results can be summarized as follows:

- Order and precipitation phenomena in Nimonic 75, which are both diffusion-controlled, were found to be markedly dependent on cooling rate from solutioning temperature. Slow cooling produced copious carbides and a fairly ordered state, while carbon in solid solution and a fairly disordered state are retained by water quenching.
- SRO kinetics are determined by nucleation of ordered zones, and carbon atoms in solid solution appear to delay this process.
- Coldwork destroys SRO but also produces non-equilibrium lattice defects which enhance diffusion and accelerate SRO formation and carbide precipitation during re-heating.
- The formation of SRO in the presence of high dislocation density produces a noticeable increase in hardness, while no such increase has been observed during ordering of undeformed material.
- The recrystallization of deformed material, revealed by marked hardness decrease, is delayed when carbide precipitation occurs after coldworking.

See programme, page 24.

Thema: Effect of time and temperature on crack propagation in a nickelbase superalloy (Udimet 700)

Verfasser: E.E. Affeldt and G.W. König

Vortragender: E.E. Affeldt

Firma: Motoren- und Turbinen-Union München GmbH

The effect of time and temperature on crack propagation was investigated using dwell-time experiments. Three different types of specimens were cut from hiped and forged Udimet 700-discs. Crack propagation was investigated using compact-tension specimens and rectangular specimens, simulating short pennyshaped corner- or surface cracks in the bore of turbine engine discs. The influence of time on crack velocity was studied using sinusoidal and trapezoidal waveforms with frequencies ranging from 10 Hz to 5 minutes at temperatures from room temperature to 923 K.

It was found that loading rates are more damaging than dwell times at maximum load. Based on a linear superposition model for different contributions to crack propagation, the influence of the loading rate is proportional to the square root of the loading time. Dwell times lead to additional but minor crack accelerations. There is some indication that they follow a linear relationship with time. Fracture surfaces were partly or totally intergranular and could be correlated to the extent of acceleration. Intergranular  $\gamma$ -particles are surrounded by the propagating cracks.

The results agree with a crack growth mechanism whereby the buildup of oxides by diffusion of oxygen along grain boundaries in front of the crack occurs during loading, and breaking of the oxides occurs during load reversal. Crack acceleration by oxidation is the main contribution to crack propagation in the temperature range 473 K to 923 K. There are additional effects at lower temperatures.

See programme, page 25.

THERMAL-MECHANICAL FATIGUE OF AN ALUMINIDE  
COATED NICKEL-BASE SUPERALLOY

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Aluminide coatings are widely used to protect jet engine blades from aggressive environment owing to their good resistance to oxidation. The mechanical properties of coated superalloys however are not so well documented at high temperatures and the thermal-mechanical loading of actual components is seldom accounted for.

This paper reports the preliminary results of an investigation of the thermal-mechanical fatigue (TMF) behaviour of aluminide coated IN 100, a blading cast nickel-base superalloy. T M F tests were conducted on an own facility which used a micro-computer to impose simultaneously a strain and a temperature cycle on a specimen. Hollow specimens were used which were given an internal and an external coating by SNECMA.

Axial strain was under closed loop control and the 3 min long T M F cycle was as follows : the temperature varied linearly with time between 600 and 1050°C and a piecewise linear variation of mechanical strain with time resulted in a maximum compression on heating at 900°C and a maximum tension on cooling at 700°C (with zero strain at 600 and 1050°C). The fatigue life range 50 to 5000 cycles was investigated. Metallographic observations were made on specimen surface as well as on longitudinal sections using scanning electron microscopy ; studied specimens were run to test completion or to mid-life.

Damage mechanisms of the aluminide coating and in particular, early crack growth mechanisms are found to be dependent upon T M F strain range. Comparison with T M F results on bare IN 100 specimens suggests that the aluminide coating can improve TMF life especially at low strain levels. This behaviour is tentatively discussed using metallographic observations.

Financial support by SNECMA is gratefully acknowledged.

See programme, page 25.

EFFECT OF HOLD TIME ON THE LOW CYCLE FATIGUE BEHAVIOUR OF  
NIMONIC PE 16

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- (d) Hahn-Meitner-Institut, Berlin

The influence of hold time at the peak tensile strain on the low cycle fatigue behaviour of a nickel base superalloy Nimonic PE 16, has been investigated. The material containing gamma prime particles of average diameter 21 nm and volume fraction 7% has been tested in air at a temperature of 923 K under fully reversed ( $R = -1$ ) total strain controlled conditions and at a constant strain rate of  $4 \cdot 10^{-3} \text{ s}^{-1}$ . The strain range was varied from 0.8% to 5.2% and hold times in the range 5 sec to 600 sec were employed. The microstructure of deformed specimens was examined with the help of transmission electron microscope and the damage and fracture behaviour using light optical and scanning electron microscopes. The imposition of hold time was found to lower the fatigue life under most conditions. The decrease in life increases with increasing hold time. It also causes increased cyclic strengthening and homogenises the dislocation distribution. The fracture mode changes from transcrystalline to essentially intercrystalline and considerable amount of grain boundary damage develops. The influence of hold time is discussed in the light of these microstructural observations.



See programme, page 25.

#### Thermomechanical Fatigue of Nimonic 80A

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The effect of thermomechanical fatigue (TMF) on high temperature damage mechanisms and cyclic lifetime of the  $\gamma'$ -strengthened Ni-base alloy Nimonic 80A was studied using a new type of TMF cycle. Applying alternating phases of athermal plastic deformation (at low temperature) and creep (at high temperature) allows a simple physical interpretation for the effects of each phase, which is not possible for conventional (in-phase and out-of-phase) TMF tests. As the new cycle type closely approximates certain service conditions, it is significant that the corresponding cyclic lifetime  $N_f$  is much lower than in asymmetrical isothermal LCF tests.

In this new type of TMF experiment the specimen is subjected to alternating changes of constant load levels and temperature. The plastic strain range  $\pm \epsilon_p$  is kept constant by compensating for thermal expansion and elastic strain. Initially, the specimen is held at a low temperature  $T_C$  and deformed in compression at a high strain rate up to  $-\epsilon_p$ . It is then heated to a temperature  $T_T$  under a small load  $\sigma_H$ , which produces no plastic strain. Subsequently, a tensile stress  $\sigma_T$  is applied and the specimen creeps up to  $+\epsilon_p$ , whereupon the stress is reduced to  $\sigma_H$  and the specimen is cooled down to  $T_C$ . The cycle is repeated until failure of the specimen.

The cyclic lifetime  $N_f$  in such a TMF test is lower by a factor of 3 to 5 compared to that in an asymmetrical isothermal LCF test performed at the same  $\epsilon_p$ . The reduction factor of  $N_f$  is more pronounced at smaller  $\epsilon_p$ . The temperature  $T_C$  hardly affects  $N_f$  for  $T_T - T_C > 100K$ . On the other hand, the sign of  $\sigma_H$  has a significant effect on  $N_f$ ; a positive  $\sigma_H$  leads to much smaller  $N_f$  values compared to a negative one.

The fractured TMF specimens contained internal grain boundary cracks similar to those found in asymmetrical isothermal LCF tests. In addition, the TMF cycle produces numerous small round cavities at grain boundary carbides. Their morphology closely resembles that of cavities caused by cold deformation and subsequent annealing under stress, where the cavity nuclei produced by the cold deformation are able to grow under the influence of tensile stresses at grain boundaries perpendicular to the stress axes.

The cavities in TMF specimens form in a similar manner. While intergranular cracks in isothermal asymmetric fatigue tests propagate through grain boundaries which contain very few cavities, the heavily damaged grain boundaries in TMF specimens accelerate the growth of these cracks. Thus additional cavitation is responsible for the pronounced decrease in  $N_f$ .

It is apparent that the combination of even very small cold deformations and high temperature creep can lead to premature failure of superalloy components in service at high temperature.

See programme, page 25.

## STEELS FOR HIGH TEMPERATURE APPLICATIONS

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Ferritic and austenitic steels have been used for many different high temperature applications in oil and chemical plants and in power generation equipment. Such applications have been generally successful, and there are many examples of successful operation at high temperatures for times well in excess of 150.000 h, however, there are particular characteristics of these two classes of material which severely restrict their range of application in terms of permissible operating parameters and these, if infringed, can lead to failures in service. The problem essentially is that for some characteristics, whether it be toughness, strength, or environmental interaction, these materials show too little tolerance to minor variations in chemistry, heat treatment, fabricating process, or operating parameters.

This paper also includes recent developments to improve the strength of steels for piping, headers and turbine rotors and the strength and corrosion resistance of boiler tubing.

See programme, page 25.

SOME 12 % Cr STEELS DEVELOPED FOR  
FOSSILE STEAM TURBINE HP AND MP PARTS

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The paper is devoted to some 12 % Cr steels operating or able to operate at 550-600°C in steam turbines. Only blades, nozzles and rotors will be considered.

Blades : The material presently used is a 0.20 % C - 11 % Cr steel with additions of Mo, Nb and V, treated to a 0.2 % YS at 20°C  $\geq$  735 MPa. The creep behaviour is of outstanding importance. As a matter of fact, the scatter of creep properties can be very extending. As this situation did not meet any clear metallurgical explanation, it was necessary to develop high temperature short term acceptance tests in order to ensure a satisfactory service behaviour. They include : 1) tensile tests completed by holding under high stress ; 2) constant strain rate (CSR) tensile tests. CSR tests prove convenient and precise a research tool for quantifying the effects of metallurgical variables.

Nozzles : The choice of suitable materials for manufacturing nozzles has a direct influence on the design. In our conception a wide use of welding is made. A 0.10 % C, 12 % Cr with additions of Mo, W and V has been developed by Alsthom and is now backed-up by a long industrial experience. The structure is duplex (50 % ferrite - 50 % martensite). The paper gives the relations between heat treatment and properties. Long term creep tests show that the material can be favourably compared with steels such as DIN X 20 Cr Mo V 12.1. The weldability is very high, such as joints can be obtained with moderate preheat temperature or even without preheating at all.

Rotors : HP rotors are manufactured presently with conventional low alloy Cr-Mo-V steels. However, in order to improve metallurgical homogeneity and creep properties at temperatures higher than 550°C, an extending research program has been set up on 12 % Cr steels hardened by Mo, Nb, V and N additions. The main results, including long-term creep tests, will be presented. The limitation of trace element contents (P, Sn, As, Sb) allows a significant improvement of ductility and toughness to be achieved without affecting high temperature properties.

See programme, page 26.

#### Steels for High Temperature Applications

- Dr.-Ing. Gerhard Kalwa, Mannesmann Forschungsinstitut -

The operating conditions prevailing in power plants and chemical plants place severe demands on the mechanical properties and corrosion resistance of the materials for components operating at high temperatures.

The constant desire to improve the power plant efficiency has led to ever increasing steam temperatures (650 °C) and pressures. Starting from plain carbon steels and low-alloy steels, materials research has led to the development of 9 % and 12 % chromium steels as well as Cr-Ni austenitic steels, the new versions of which exhibit also high nitrogen contents.

In the field of coal conversion - coal gasification and coal liquefaction - the resistance of materials to corrosion at temperatures ranging up to 1000 °C, even in gases containing aggressive species such as  $H_2$ ,  $H_2S$  and  $SO_2$ , plays a crucial role. In addition, the materials need to possess adequate creep strength. Low-alloy pressure vessel steels ranging up to 12 % Cr steels can be used satisfactorily in coal liquefaction plants, where the operating temperatures are below 500 °C. But, austenitic steels with chromium contents in excess of 25 % are required for components of coal gasification plants with high operating temperatures. A similar situation also exists in the field of high temperature chemical plants.

Since the high temperature equipment is to be designed on the basis of time-dependent strength values (creep rupture strengths at 200 000 hrs. are needed in the design of power plant components), the development of materials for these applications is time-consuming and hence very expensive. Therefore, materials for high temperature applications in the year 2000 must be available already now so that there is enough time for carrying out the qualifying tests before they can be put in actual service.

See programme, page 26.

Powdermetallurgical Fabrication of Steam Line Components  
from Advanced 9-12 % Cr Steels

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U. Heisel, TECHNISCHER ÜBERWACHUNGSVEREIN, BADEN E.V.,  
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Net shape fabrication of parts with complex geometry starting from powder has come a long way. Nowadays, components produced from powders can be considered 100 % dense thanks to compaction by hot isostatic pressing (HIP). As the processing cost decreases and large HIP-units become available, there is every indication that the method can be applied for the economic manufacture of large complex shape pressure vessels like steam valves and steam collectors.

The subject is settled in a more general context concerning the identification of improved martensitic 9-12 % Cr steels for application in future steam power plants which are supposed to have higher operating temperatures and steam pressures than apply for present designs. In particular, for components made from these high grade steels, integral fabrication procedures like powder metallurgy (P/M) may satisfy the required uniformity of properties in a better way than conventional fabrication i.e. welding.

The paper highlightes recent results of a joint European project (COST) on the approval of a steam collector produced from 9-12 % Cr steels (X20CrMoV121 and T91) by powder metallurgy. After specimen collectors had been tested non-destructively, they were sectioned and subject to mechanical testing. Creep testing of P/M-X20CrMoV121 has reached now 40000 hours, creep data of T91 covers about 10000 hours. A special low cycle fatigue test rig was used to simulate real service conditions by actuating the collector nipples at their position. The project is still in progress, the results look promising. New P/M-fabricated high grade martensitic steels are now considered.

See programme, page 26.

The influence of precipitated carbides on toughness  
properties of X 20 CrMoV 12 1

by

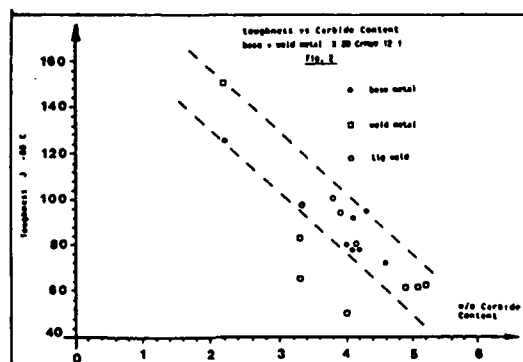
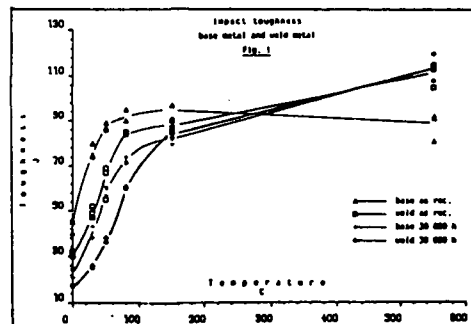
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\*\*\*

The ferritic 12 % Chromium steel X 20 CrMoV 12 1 (Mat.Nr. 1.4922) is widely used in Germany as material in high temperature steam application. Under operating conditions the material exhibits a loss in impact and fracture toughness (Fig.1). This decrease in toughness was studied basically on thermally treated materials at 550 °C with particular emphasis on the role of carbide precipitation. For comparison a few creep tested samples (550 °C) were included.

The study indicated, that the loss in toughness could be correlated to the amount of precipitated carbides (Fig.2). Approximately 50 % of these precipitates could be dissolved in the matrix during tempering at 750 °C, thus restoring high impact properties, as observed in the as received condition.

It appears, that carbide precipitation is influenced by stress, because creep tested material exhibited almost no change in carbide content as compared to thermally treated material.



See programme, page 26.

High temperature materials in fossil fuel conversion technology

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Construction materials play an important role in the development of advanced fossil fuel conversion and utilization technologies and they often operate at the limit of their capability.

The main processes for the conversion of fossil fuels will be described: combustion, gasification, liquefaction and pyrolysis. The modern installations are both numerous and complex with fluidized bed techniques being the most popular. The materials characteristics (physical-chemical and mechanical) have to satisfy very high technical demands to guarantee reliable and safe operation.

The materials selected include high temperature steels, superalloys and coated materials; hints will be given into engineering ceramics 'heat exchanger' applications.

The severe operating conditions call for a good knowledge of their conduct in the face of multiple degradation reactions e.a.:

- High temperature oxidation, carburization and sulphidation etc.,
- Hot corrosion by fused salts,
- Corrosion-erosion,
- Mechanical behaviour: creep, fatigue at high temperature in corrosive environments.

Materials failure mechanisms will be described and theories developed for the prediction of component lifetime in modern installations.

A materials selection guide for advanced energy conversion technologies will be prepared and new developed materials highlighted.

Pointers are given for the direction of future research and development for high temperature materials to meet this growing technological challenge.

See programme, page 27.

**STATE OF THE ART AND FUTURE PROSPECTS  
FOR  
HIGH TEMPERATURE COMPOSITES**

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The interest and activities in the research and development field of reinforced carbon and ceramics are increasing. This interest comes from the potentialities and rising promises that these composites represent to meet requirements of thermostability, reliability and specific performances that today's projects of aeronautical and spacial systems impose.

Beyond reliability parameters, toughness, damage stress levels, thermochemical resistance and cost are now determinative for further developments and uses.

After an analysis of the microstructural rupture of these composites and of the evolution models describing this rupture and the new micromechanical methods, the present paper:

- develops the mains aspects of protected reinforced carbon and ceramic processing linked to their new functionalities.
- gives some examples of realization,
- approachs some future prospects.p



See programme, page 27.

**Fracture behaviour of ceramic-ceramic composites and related toughening mechanisms**

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During fracture of a ceramic composite there is sliding at the fibre-matrix interface and the complete failure is in most cases accompanied by fibre pull-out. The fracture surfaces exhibit variable pull-out lengths depending both on the statistical strength of the fibres and on the characteristics of the interface. The crack bridging and finally the work of fracture are largely governed by the pull-out process.

The aim of the present paper is to describe firstly the different mechanisms which are working during the crack growth (matrix cracking, fibre failures at given locations, pull-out, ...), in relation with the resulting fracture surfaces. Secondly, the mechanisms are analyzed in relation with micromechanical parameters (statistical fibre strength, critical shear stress at interface, measured by indentation) and with more macroscopic characteristics (crack growth resistance or work of fracture). Examples concerning 2D SiC-SiC composites from S.E.P. (France) are presented.

See programme, page 27.

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CERAMIC  
COMPOSITES

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Different whisker toughened materials have been subject to microstructural study, with the objective of identifying the mechanism that provides the major contribution to toughness. It is concluded that, for composites with randomly oriented whiskers, bending failure of the whiskers obviates pull-out, whereupon the major toughening mechanisms are the fracture energy consumed in creating the debonded interface and the stored strain energy in the whiskers, at failure, which is dissipated as acoustic waves. The toughening potential is thus limited. High toughness requires extensive pull-out and hence, aligned whiskers with low fracture energy interfaces.

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## **Tribological Properties of Engineering Ceramics**

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Monolithic, oxide, nitride and carbide ceramics offer high hardness and high resistance to thermal and corrosive loadings combined with relatively low densities. There are substantial advantages over metallic materials for use in structural applications. Ceramic materials are increasingly used for wear resistant parts. This leads to a great interest of engineers and other users in tribological behaviour of modern engineering ceramics and especially compared with metallic materials. Low and high values of coefficient of friction and wear rate of ceramics are reported as a function of the environmental conditions. Hardness may be an important property for metals, but what about hardness or porosity of ceramics in sliding pairs? These and other questions have to be answered for a successful application of ceramic materials in tribological practice.

The paper presents experimental results of wear and friction behaviour of ceramics such as  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{TiO}_5$ ,  $\text{ZrO}_2$ ,  $\text{SiSiC}$  and  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  with and without an open porosity. Tests were carried out dry, oil lubricated and water lubricated using a pin/ring-tribometer at room temperature in laboratory air. Sliding pairs of self-mated and dissimilar ceramics and also ceramics and steels in contact with a hardened 0.6 % carbon steel were studied.

Scanning electron microscopy and energy dispersive X-ray analysis revealed different wear mechanisms depending on the materials and experimental conditions. Plastic deformation, material transfer, tribochemical reaction, grooving and microfracture were observed on worn surfaces. The results show that ceramics may be better than steels but their tribological behaviour is strongly influenced by the operating conditions.

See programme, page 28.

## SOME RECENT DEVELOPMENTS ON SUPER- PLASTICITY OF CERAMICS

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Structural superplasticity in fine grained single or multiphase ceramics has been reported for several years, although superplastic-like behaviours were recorded much earlier, but not recognized as such.

At least two reviews on the subject have been published, the latter one as recently as in the summer of 1988. They will be reminded of and this presentation will build from them.

Although virtually any polycrystalline ceramic should exhibit high ductility when sufficiently fine grained and under appropriate testing conditions, attention at the moment appears mostly focussed to  $ZrO_2$  and  $Al_2O_3$  based materials, either presumed to be single phased or as two phase composites. Two main lines of effort can be indentified and will be discussed in turn.

On the one hand, basic phenomena and micromechanisms associated with or responsible for superplasticity are under investigation. Constitutive creep equations are being established under both compressive and tensile conditions, and elongations in excess of several 100 % are commonly accessible with  $ZrO_2$ - $Y_2O_3$  alloys (Y-TZP) at  $\sim 1400 - 1500^\circ$ . Residual impurity effects are especially of concern, in particular as they may influence the defect structure of the material or give rise to intergranular glassy films thus exerting a role on deformation. Microstructural changes taking place during deformation, e.g. grain growth, cavity formation, texture development also are under scrutiny. And for the  $ZrO_2$ - $Y_2O_3$  system solute redistribution possibly leading to phase transformation during testing also has been brought to attention.

On the other hand preliminary investigations oriented more toward applications are under way. First, it may be possible to extend conventional hot-pressing to more intricate geometries via some sort of sinter-forging approach. The application of properly designed shear stresses may be beneficial to densification and yield useful material flows. Second, superplastic forming in a similar way to what is done with metals may also be attempted starting from predensified shapes. Some encouraging results have been obtained but major practical problems remain to be solved notably with lubrication and tooling. Finally, it appears feasible to develop ceramic joining techniques that would rely upon superplastic properties. In this way ceramic parts of similar compositions could be assembled by some sort of hot loading whereas the same should hold for those dissimilar materials having compatible thermal expansions. Illustrative examples for each of these three processes will be presented.

See programme, page 28.

Resistance of ceramics to thermal shocks

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Ceramic materials exhibit a brittle behaviour. Therefore, they are sensitive to differential strains, such as those which are induced by thermal shocks and thermal fatigue. Thermal shocks cannot be avoided in thermal machines, a field in which new engineering ceramics show interesting potentialities.

This paper summarizes the thermal shock properties of ceramics, taking account two complementary approaches : the "thermo-elastic theory", which focuses on the initiation of newly created cracks, and the energetic theory (Hasselman's theory), which focuses on the propagation of pre-existing flaws.

Various experimental cases are discussed. The use of non-destructive evaluation methods is detailed. The needs for a standardization of experimental methods is pointed out.

See programme, page 28.

## **Composite Ceramics from Polymer-Metal Mixtures**

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Ceramic Matrix Composites (CMC) in the quinary system Me-Si-N-C-O, with Me = Ti and other Group IV-VI elements, were prepared by a novel processing route from polymer-metal mixtures.

Non-reactive ceramic and reactive metallic fillers were dispersed in polymer solutions of polymethylsiloxane, polymethylphenylsiloxane and polyethylsilazane. During pyrolysis at 800 to 1200°C the metallic filler particles react with the decomposition products of the polymers to form carbide or nitride phases in a silica or siliconoxynitride matrix. The forming of the polymer-filler precursor systems into complex shapes may easily be achieved by well-established plastic forming techniques, e.g. thermopressing. Thermodynamic calculations were used to predict the conditions for the formation of the appropriate carbide and nitride phases, dependent on the condensed and gas phase compositions. The mechanisms and kinetics of the filler-matrix reactions during pyrolysis were investigated by XRD, SEM, and Thermal Analysis in order to control microstructure development.

The novel CMC materials offer excellent forming properties, near net-shape capability, and low-temperature processing. Various types of composites, including particle- and fiber-reinforced ceramics, ceramic bonded hard materials, and polymer or metal infiltrated ceramic composites are possible.

See programme, page 28.

#### SOL-GEL DERIVED CERAMICS

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The sol-gel process is gaining more and more importance for ceramic powders, films, fibers and as binders. The main advantages are the purity of the raw material and the possibility of tailoring intermediates for special processing technologies. Thus, the particle size and distribution can be established in a wide range and especially small particles can be synthesized, even down to the nanometer range. Viscous precursors can be prepared for fiber drawing, coating and thin sheet formation. The sintering activity of sol-gel derived raw materials can be substantially lower than those of conventional powders. In order to use this potential for making good ceramics appropriate processing technologies, e.g. avoiding agglomeration during drying and calcination by adequate surface chemistry, development of high solid content sols for low shrinkage precursors for sheet and fiber fabrication or infiltration are necessary as well as powder coating techniques for homogeneous distribution of additives. In order to reduce costs, the use of precursors cheaper than alkoxides has to be developed. This can be achieved, for example, by water in oil emulsion techniques. A survey over several sol-gel techniques with special emphasis on the processing step and selected examples are given.

See programme, page 29.

### ***Carbons for biomedical applications***

R. RANC and D. MAZIERE

Carbons used in biomedical applications for their hemocompatibility, are less organised, less crystalline forms than graphite or diamond. They are called isotropic, turbostratic carbons. Structural and physical properties of these carbons are mentioned. Hemocompatibility is also pointed out.

Two types of medical applications are developed in the CENG/DMG laboratories :

- in cardiovascular applications, the extremely rare material which does not induce thrombosis and hemolysis is used : the isotropic pyrocarbon ;
- in orthopaedic applications, the very peculiar mechanical properties of pyrocarbon are developed.

#### ***Cardiovascular applications :***

A french mechanical cardiac valve is studied by the CENG ; the design has been proposed by Professor CARPENTIER's medical team. The valve has two semi-circular leaflets slightly concave for a better liquid flowing and a full opening during this flowing. Some prototypes have been manufactured and are tested :

- in vitro, with a test bench allowing to study their mechanical and hemodynamical performances ;
- in vivo, on goats.

Industrial transfer step just has begun.

#### ***Orthopaedic applications :***

A finger prosthesis has been studied in accordance with a Grenoble CHRU medical team. The rubbing properties and the wear resistance of pyrocarbon have been used to obtain a very reliable product. Manufacturing of prototypes is in progress.

Beside the hemocompatibility of the isotropic pyrocarbon, some other forms of carbons show an excellent biocompatibility : for instance, glassy carbon and C-C composites don't provoke the usual rejective reactions in contact with soft tissues and bone (absence of encapsulation) and can be envisaged as implants material.

Let's add that with deposition processes at low or even ambient temperature (physical vapor deposition), it's possible to coat metallic (titanium alloys) and polymeric implants (fabrics) which keep their elastic properties.

The pyrolytic carbon and others turbostratic forms, are, with no doubt, going to play an increasing role in future developments of the implantology.

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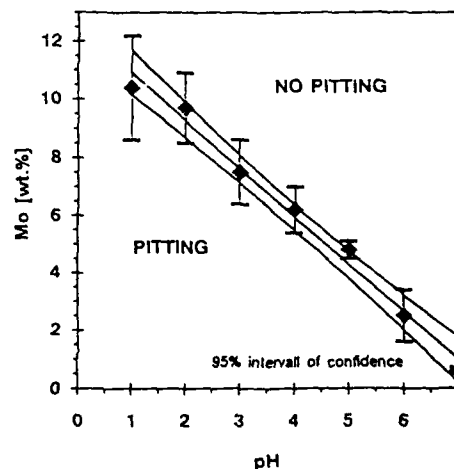
See programme, page 29.

EFFECT OF MO-CONTENT AND PH ON PITTING CORROSION OF NI-CR-MO DENTAL ALLOYS.

J. Geis-Gerstorfer<sup>1</sup> and E. H. Greener (University of Tübingen and Northwestern University of Chicago)

Nonprecious alloys on a Ni-Cr basis have already been successfully employed in prosthetic care for many years. If one considers the chemical composition of the Ni-Cr-alloys which are currently on the market one finds a widely diversified spread in composition (Ni=60-82 wt.%, Cr=11-25 wt.%, Mo=0-14 wt.%), which has consequences as regards the corrosion resistance of the respective alloy. The goal of this study is to examine the effect of varying Mo-content on the passivation behaviour of Ni-20Cr-Mo under varying clinically relevant electrolyte conditions as a function of the pH value.

With the aid of cyclic polarization measurements the passivating behaviour of 6 highly pure experimental Ni-20Cr-Mo alloys with Mo content between 0 and 10 wt.% was examined in de-aerated buffered 0.1 M NaCl solutions with pH values between 1 and 7. The pitting potential  $E_p$ , the critical pitting potential  $E_c$ , the current density  $i_{0.3}$  at 0.3 V(SCE), as well as the PRE-values (pitting resistant equivalent) which were obtained from linear regression analysis ( $p < 0.05$ ) of  $E_p = E_p(\%Mo)$ -curves, were used as evaluation criteria. The resistance against pitting corrosion in acid milieu was immensely improved by increasing Mo content, while in neutral milieu approximately unchanged pitting potential  $E_p$  was found. If one assumes, with reference to the oxidation potentials which have been measured for the mouth, that the pitting potential  $E_p$  of dental alloys should not lie under 0.3 V(SCE), then at pH 1 this requirement is fulfilled at a PRE value of 93. At pH 2 the PRE value should lie above 64, at pH 3 at more than 51, at pH 4 higher than 43 and at pH 5 and 6 above 30 and 21. At pH 7 all  $E_p$  values lie above 0.3 V. The required minimal content of Mo for the prevention of pitting has been calculated from the slope of  $E_p = A + B \cdot pH$ . In order to prevent pitting of Ni-20Cr-Mo dental alloys the minimal Mo-content necessary (see figure) can be calculated using the formula  $\%Mo \geq 12.6 - 1.66 \cdot pH$ . This study was supported by DGZMK.



See programme, page 29.

Indium in Dispersed Phase Amalgams:  
Effect on Properties and Mercury Vapor Release

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The effect of In on the compressive strength, flow, and Hg vapor release of dispersed phase, dental amalgam alloy is investigated. Indium powder and Ag-Cu eutectic (72%Ag-28%Cu) powder (dispersion phase - DP) were admixed with conventional-type dental alloy powder (matrix - M), the latter of composition 69%Ag-26%Sn-4%Cu-1%Zn, to form a powder composite. Amalgam specimens were prepared by triturating requisite amounts of Hg and powder composite in an amalgamator. The amalgam was condensed in a cylindrical mold, 4mm dia x 8 mm, and the compressive strengths determined for a strain rate of 0.020 cm/min. Figures 1 and 2 show that the optimum amount of DP and In in the powder composite are approximately 42% and 10% respectively, giving 1 hr and 24 hr strengths of 162 MPa (23,500 psi) and 567 MPa (82,200 psi) respectively.

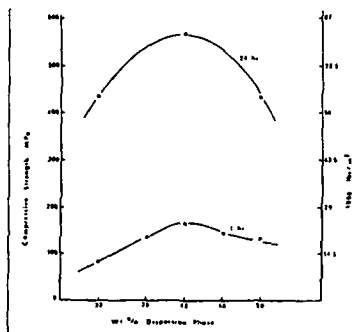


Fig 1 Compressive strength of amalgam vs. dispersion phase content of powder composite containing 10 per cent indium. Condensation pressure 68.94 MPa (10,000 psi). Mercury/alloy trituration ratio, 0.75/1.

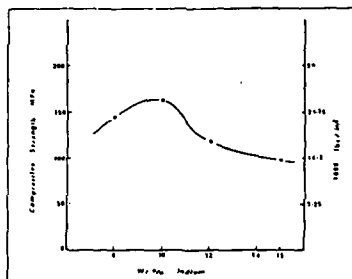


Fig 2 One hour compressive strength of amalgam vs. indium content of powder composite containing 42 per cent dispersion phase. Condensation pressure 68.94 MPa (10,000 psi). Mercury/alloy trituration ratio, 0.75/1.

Table 1 shows that flow (creep) increases with In and decreases with DP amount, and that 42-50% DP is required to counter the flow increase resulting from the addition of 10% In. For the Hg release determinations, the amalgam specimens were condensed at 14 MPa (2030 psi). Following preparation, the specimens were immediately placed in stoppered vials, and then periodically removed and tested for Hg release using a United Technologies, model MV2 mercury detector. Table 2 shows that the In additions greatly reduce Hg vapor release from amalgam. The results are discussed in relation to the phase relationships for In alloys, and the thermodynamics of the In-Hg system.

Table 1. 21 Hr Flow of Amalgams at 37°C and 10.25 MPa (1500 psi). Condensation Pressure 68.96 MPa (10,000 psi).

Powder Composite			Hg/Alloy	Flow
XM	ZDP	ZIn	Wt Ratio	%
67	33	0	1/1	0.37
57	33	10	1/1	0.90
57	33	10	0.75/1	0.70
48	42	10	0.75/1	0.40
40	50	10	0.75/1	0.37

Table 2. Mercury Release From Amalgams Vs. Time After Preparation. Condensation Pressure 14 MPa (2030 psi).

Powder Composite			Hg/Alloy	Hg Release		
XM	ZDP	ZIn	wt ratio	(μg.m <sup>-3</sup> )		
				1hr	2hr	3hr
67	33	0	1/1	485	220	80
48	42	10	0.75/1	44	21	10
44	42	14	0.75/1	19	9	7

See programme, page 29.

STUDY OF METAL-CERAMIC INTERFACE FOR DENTAL APPLICATIONS

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J. BRUGIRARD - Faculté Dentaire de Lyon - FRANCE

This study was aimed at characterizing the metal/ceramic interface, of non precious ceramic coated dental alloys, used in odontology for esthetic reasons.

Micromecanic properties of the ceramic/metal joining have been valuated by means of wrenching in traction and rupture in bending tests, which gave an acceptable agreement of the results. These tests allowed particularly to compare the influence of the base alloy composition and of the surface preparation before ceramic deposition, on the cohesion at metal/ceramic interface.

Several surface analysis methods have been used to study the adhesion mechanisms at interface. They led us to state the influence of the diverse occurring processes - diffusion, oxidation, combination of concerned chemical elements - and to determine the components having an active effect in the elaboration of the interfacial bonding.

See programme, page 30.

#### A NEW FATIGUE RESISTANT PROSTHESIS SURFACE

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The surface of prosthesis for hip and knee joint substitutes have to have a certain roughness for better ingrowth into bone. There are for example surfaces coated with layers of small spheres and porous surfaces which improve bony contact. However, every roughness consists of surface notches at which cracks may be initiated due to notch stresses. The aim of the new surface introduced is to guarantee the same good bone-prosthesis contact but without any notch stresses. The latter requirement is satisfied by a well-defined shape of the grooves between the individual prosthesis spikes. This shape has been optimized by a new method of 'Computer Aided Shape Optimization' (CAO) based on the principle of tree growth. This method is described in [1,2] where it is also shown that trees optimize themselves in order to avoid any notch stresses in the tree design. In this sense a design proposal for the prosthesis surface was made and it was shape-optimized by computer-simulated biological growth (Finite Element) until the notch stresses disappeared.

#### References:

- [1] C. Mattheck  
Ein 'intelligentes' CAD-Verfahren auf der Basis biologischen Wachstums zur Streckung der Rißinitiierungsphase technischer Bauteile  
Lecture and Proceedingscontribution at the 21st Meeting of the DVM - working group 'fracture' Bad Nauheim 27./28. Feb. 1989
  
- [2] C. Mattheck, S. Burkhardt  
Computer aided shape-optimization based on biological growth  
Lecture and Proceedingscontribution of the STRUCOPT - 89 Conference, Paris 23.-25. May 1989

See programme, page 30.

# EFFECT OF IONIC IMPLANTATION ON THE TITANIUM ALLOY-POLYETHYLENE FRICTION COUPLE IN JOINT PROSTHESES

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Joint prostheses are usually composed of a metal stem with a friction surface in contact with a polymer part. Because of the satisfactory fatigue-corrosion resistance of titanium alloys in chloride solutions, they tend to supplant stainless steels and chromium-cobalt alloys for biomedical applications. However, their very bad wear behaviour, even with a soft material like a polymer, makes them unsuitable for a friction couple in hip or knee prostheses. This is the reason why many titanium stems are associated with ceramic parts. In hip prostheses, for instance, an alumina or zirconia ball is fitted on a conical stem. Another answer to this problem consists in surface treatments of titanium alloys. Ion nitriding could be interesting, but it produces bulk structure modifications which involve a drop in fatigue strength. Dimensional changes also occur which are not compatible with geometrical specifications. PVD coatings are developing, but do not seem presently to offer a sufficient guarantee.

Ion implantation is a surface treatment which is performed at a temperature close to room temperature by introducing into a thin layer of the material a large quantity of accelerated ions. The structure is highly modified, but only in the first tenths of a micron underlayer. New phases and residual stresses generally induce better wear resistance in metals. For polymers, ion implantation has principally been used for electric conductivity modifications. Few papers report on mechanical property variations.

We have studied the effect of nitrogen ion implantation on structure and mechanical property modifications in the TA6V4 titanium alloy and on a UHMW polyethylene. For comparison on the mechanisms of wear, we shall give some results on nitrogen ion implantation in the 316L stainless steel in friction with polyethylene. Low angle X-ray diffraction and LDS have been used for metal structure analysis, while ESCA, ATR IR, wettability and nuclear reaction were used for polymer surface characterizations.

Materials have been tested on two different devices : a pin-on disc system with a continuous, unidirectional friction, and a ball-socket system with two alternative, crossed rotations. In the two cases, the average pressure, relative velocity and lubricant were the same. They are similar to those encountered in human joints.

Nitrogen ion implantation in TA6V4 and UHMWPE highly improves their friction behaviour under conditions closed to those of joint prostheses in the human body. Wear of the polymer cup can be divided by a factor of 25 if the two materials are surface treated. Two mechanisms of wear of titanium alloys in contact with polyethylene are described which can explain different behaviours in a hip or a knee titanium prosthesis. After surface treatment, the surface of the metallic specimens (discs or spheres) wear is so little that it must be measured by radioactivation methods. Although the very thin layer modified by ion implantation ( $2\text{ }\mu\text{m}$ , for instance), the nitrogen distribution in titanium is practically the same after more than 4 million cycles in the pin-on disc friction device.

This improvement of wear resistance is correlated to structural modifications in the TA6V4 alloy and in the UHMW polyethylene.

See programme, page 30.

Optimization of ODS-Niobium for load-bearing implants  
with excellent biocompatibility

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The excellent biocompatibility of niobium has hitherto been hardly exploited because of the drawbacks in the mechanical properties of the pure metal. Conventional alloying to reach higher strength levels should be avoided in order to keep biocompatibility at the level of the pure niobium. Other important demands to be met are high fracture toughness, good fatigue properties and ductility.

These goals have been met by using a proprietary P/M process to get an oxide-dispersion-hardened niobium with a very fine and homogenous dispersion of  $\text{TiO}_2$ . This optimized oxide dispersion leads to favourable room-temperature mechanical properties inspite of the small amounts of oxide used (about 0.5 wt.%).

With the proper optimization measures, the following data have been reproducibly achieved:

R.T.-Tensile strength:	$> 1000 \text{ N/mm}^2$
Elongation:	$> 10 \%$
Fatigue strength:	$> 450 \text{ N/mm}^2$
DBTT:	ca. $-50^\circ \text{C}$
$\text{TiO}_2$ mean diameter:	60 Å
Mean particle spacing:	360 Å

The peculiar mechanism working to get  $\text{TiO}_2$ -dispersoids with mean diameters of ca. 60 Å and the measures used to optimize the microstructure of Nb- $\text{TiO}_2$ -alloys shall be discussed. Results of a wide range of analytical methods including TEM with quantitative image analysis, SEM and in-depth chemical analyses were used to clarify the underlying mechanism and to optimize the oxide-dispersion-strengthening of niobium.

Applications for this high-strength, but nevertheless ductile and biocompatible Nb- $\text{TiO}_2$  alloy are among others seen in the field of high-load bearing medical implants. First results from animal tests of bone-plates and bone-screws shall be presented.

See programme, page 30.

**MECHANICAL AND CHEMICAL PROPERTIES  
OF Ti/Al<sub>2</sub>O<sub>3</sub> JOINTS FOR DENTAL IMPLANTS**

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Ti-Ta and Ti-Nb alloys were diffusion bonded in a high vacuum to a 99.7 w/o alumina ceramic. The composition and microstructure of the metal part of these metal/ceramic joints were optimized with respect to requirements of composite dental implants. The microstructure of the Ti alloys bonded to the ceramic is subdivided into a reaction double layer containing the phases TiAl and Ti<sub>3</sub>Al, a transition region of coarse  $\alpha$ -Ti and  $\beta$ -Ti plates and the bulk ( $\alpha$ + $\beta$ ) Ti. The metal part of the joint was modified by annealing at 800 °C/1h after bonding and during cooling down. Thereby a refinement of microstructure was obtained. By lowering the bonding temperature down to 900 °C ( $\alpha$ - $\beta$ )-transformation of the Ti alloys was suppressed.

Optimized joints fabricated by diffusion bonding in a high vacuum at 1200 °C/1h from an alumina ceramic and Ti-Ta or Ti-Nb alloys containing 30 w/o Ta and 40 w/o Nb, respectively showed rather high fracture resistance values of 2.6 MPam<sup>1/2</sup> and 3.2 MPam<sup>1/2</sup> respectively.

Ti/Al<sub>2</sub>O<sub>3</sub> joints were fabricated with a thin intermediate layer of Al or Nb. The Ti/Nb foil/Al<sub>2</sub>O<sub>3</sub> joints possessed a high fracture resistance of 2.7 MPam<sup>1/2</sup>. The microstructure of the transition region adjacent to the interface resembles that of Ti-Nb/Al<sub>2</sub>O<sub>3</sub> joints. It shows a reaction double layer and a region high in Nb adjacent to it.

## CERAMIC PLASMA SPRAY COATINGS ON METALLIC JOINT PROSTHESES

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Since 1976, alumina plasma spray coatings have been used on several thousands of cementless hip and knee prostheses, for improving fixation of the stem in the bone by a mechanism of biological anchorage. When new bone cells are formed, they grow in close contact with the porous coating and increase adherence bone-prosthesis.

The results presented in this paper are relative to alumina plasma spray coatings on the 316L stainless steel and the TA6V4 titanium alloy for orthopaedic applications. The  $\alpha$  alumina powder is melted in the plasma torch and droplets are shot forward to the metal surface where they splash and cool in thin, 30-50  $\mu\text{m}$  diameter plaques. Structure and properties of the coatings have been studied by optical and electron microscopy, X-ray diffraction methods and several mechanical tests, in order to evaluate adherence stresses, elastic coefficients and residual stresses in connexion with the porosity.

The standard alumina coatings for orthopaedic applications are 150  $\mu\text{m}$  thick. Their porosity has been measured with a mercury porosimeter. About 30 to 40% of the total volume consist of voids distributed in two pore average sizes (0.1 and 30  $\mu\text{m}$ ). The first size corresponds to microcracks in the thin plaques and the second one, to the voids between the plaques. In some cases, a preferential cristallographic orientation, or texture, with a [100] direction perpendicular to the surface has been observed. The cristallographic structure is 10%  $\alpha$  alumina and 90%  $\gamma$  alumina, which can be transformed into  $\alpha$  alumina by heat treatment.

Adherence has been measured with two methods : tension on a stuck pin, and shear in a flexion test. In tension tests, fracture is mainly adhesive and the stress is about 10 MPa. In shear tests, fracture is cohesive because of the metallic substrate roughness and the shear stress is about 15 MPa. The values are the same for specimens after 6 months in the Ringer solution or for retrieved prosthetic implants.

Young modulus has been measured with two technics on the coating separated from the metal substrate by an original dissolution method. First, the alumina thin plate is loaded in flexion as a cantilever beam and Young modulus is calculated from the deflexion and load values. Second, ultrasonic wave velocity gives Young modulus at very low strains. It varies from 10 to 20 GPa, as a function of porosity, in good agreement with theoretical models. It is noticeable that these values for ceramic coatings are closed to those for cortical bone.

Residual stresses have been measured with two different methods : stress relaxation in the coating when separated from the substrate and X-ray diffraction on the coating, while on the substrate. There is a large difference between the values obtained according to the method (4 to 300 MPa) and a critical analysis is made to understand why.

A complementary research is currently made on diffusion treatments of an intermediate layer in between metal and plasma coating, and on composite coatings of progressive composition from alumina to calcium phosphates.



See programme, page 30.

### Microstructure and Strength Development in Calcium Phosphate Biocements

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Calcium phosphate-based cements are of considerable interest for biomedical applications. As biodegradable materials, they could be used for tooth healing, as well as bone grafting (1). The plasticity of freshly prepared cement pastes would make them easy to fit the shape of bone defects. Their subsequent hardening in situ would then ensure sufficient mechanical strength, for the time necessary to their resorption and replacement by new bone.

Two important properties of cements are their rate of setting and ultimate mechanical strength. These properties can be controlled by selecting carefully the nature, proportions, and processing conditions of the starting constituents.

The present communication will present some examples of calcium phosphate cement formulations, based on tricalcium phosphate (TCP) admixed either with monocalcium phosphate monohydrate (MCPM) or with dicalcium phosphate dihydrate (DCPD), to which other calcium compounds such as calcium carbonate (CC), calcium sulfate hemihydrate (CSH) and calcium pyrophosphate (CPP) have been added, either as co-reactants, or as setting regulators. In some cases, hydroxyapatite (HAp), or fluoride salts were added as seeding agents, in order to promote the crystallisation of apatite.

According to the results, the evolution of strength during aging of the pastes correlates to mineralogical changes during which newly formed crystals, either of DCPD or HAp, act as bridges between TCP aggregates. Strongly sintered TCP powders have been found to help in achieving a higher ultimate strength. Also important is not only the amount of binding crystals, but also their dispersion throughout the hardened cement, smaller numerous crystal being more efficient in promoting strength. At longer aging times, a decay of the strength has been observed in some cases, which could be ascribed to intergranular corrosion of the TCP aggregates resulting from chemical reactions between TCP and other components of the paste. In other cases, long term weakening could be ascribed to the secondary growth of the binding crystals. The results have also shown that very good strengths (1.5 to 3 MPa diametral strength) could be achieved in the most favorable cases, despite a very large porosity of the hardened cement (45 to 54 % vol). The use of CC in the formulation of the paste promoted the formation of highly porous cements.

(1) Brown W.E. and Chow L.C., Patent US 4,518,430 Oct 20, 1985.

See programme, page 31.

CERAMICS IN MICROELECTRONICS  
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A broad review of ceramics in microelectronics for processing, storing, transferring, printing, and displaying information is highlighted. Ceramic packaging is emphasized, and a review of the history, evolution, and state of the art is presented. The multilayer ceramic packaging technology capable of providing interconnections for as many as 100 chips, considered the state-of-the-art, is discussed in terms of ceramic, glass and metal materials as well as processes by which these substrates are made. The ideal properties of ceramics in terms of their electrical, thermal, and mechanical properties are reviewed. The recent developments in ceramics resulting in potentially improved thermal and electrical properties by the use of SiC, AlN, and glass-ceramics are discussed. The scientific understanding necessary to support these developments is mentioned.

See programme, page 31.

GLASS-CERAMICS IN HIGH PERFORMANCE  
MICROELECTRONIC PACKAGES

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The problems of increased power dissipation of VLSI chips, increased off-chip frequencies and the demand for hermetic packages have been addressed by the design of a glass-ceramic package incorporating a metal heat sink. This takes the form of a glass-ceramic coated metal substrate with an uncoated chip well. The same glass-ceramic is used to form the package walls, in conjunction with a metal or glass-ceramic lid.

The metal substrate is molybdenum - chosen to give a reasonable thermal expansion (TCE) match to silicon and yet be workable and economic. The dielectric coating is formulated to be compatible with molybdenum in terms of TCE match and formation of an adherent bond to the substrate. In addition, the permittivity and dielectric loss have been minimised at  $-6$  and  $<10^{-3}$  respectively.

Processing is at temperatures below  $1000^{\circ}\text{C}$  enabling the use of high conductivity, thick film inks such as Cu and Au. Interactions between the molybdenum and the glass-ceramic and between the glass-ceramic and the Cu or Au metallurgy are sufficient to give good bonding but not so extensive that electrical performance is impaired.

Fabrication procedures include screen printing of the glass-ceramic coating onto the metal substrate and tape casting of the glass-ceramic for the walls and lid. These parts can be produced separately and then glassed together. Alternatively, co-firing of substrate, metallurgy and walls is feasible.

So far, substrates of up to  $100\text{ cm}^2$  have been produced and 160 I/O demonstrators have been satisfactorily tested up to 3GHz.

This work was carried out under SERC/ALVEY project 050.

Suitable for Symposium C.

See programme, page 31.

#### **Ceramic Filled Glass Composites for Multilayer Substrates**

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Multilayer ceramic modules based on alumina have significantly increased circuit package densities and substantially reduced intra-package wiring lengths and inter-package connections while improving system performance and reliability. To realize still higher performance from a multilayer ceramic module, the electrical properties of the package materials and interconnect materials must be factored into the design. Minimizing high frequency circuit impedance is a major goal for next generation multilayer packages while fabrication and reliability improvements are equally valued. For example, further advancements in system reliability can be realized by minimizing the linear coefficient of thermal expansion differences between the substrate and the semiconductor devices. Similarly, the potential to perform metal Co-fire Technology using standard metal pastes at a ca. 500°C lower sinter temperature as compared to an alumina substrate is an attractive processing advantage.

With the aim of designing the next generation substrates, the material development goal was set to the following objectives:

1. Dielectric constant < 5
2. Thermal Coefficient of expansion = 3 ppm/°C
3. Mechanical strength > 200 MPa
4. High conductivity metallization (Au, Ag, Cu)
5. Development of Co-fire multilayer manufacturing techniques

Screening experiments showed that glass matrix ceramic composites could be designed to achieve the target properties. A low transition temperature glass, for the matrix material, with a magnesium aluminosilicate filler material achieved all the desired properties.

This paper will illustrate the "Designed Experiment" approach to help guide the design of a glass/ceramic composite system for optimal sintering properties. In addition, the importance of raw material interactions during the sintering process to control the sintering temperature, sintering rate, and softening point of the composite will be discussed.

See programme, page 31.

#### **HIPING OF ALUMINA- GLASS SYSTEMS**

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Large residual porous defects in sintered alumina ceramics with an intergranular glassy phase, can be eliminated during final stage HIPing. The pore elimination may occur by a mixed flow of the glassy phase and grains or by a the flow of glassy phase alone. The effect of applied external pressure, volume fraction and distribution of glassy phase and the effective grain size on the type of the pore filling mechanism is discussed. Increasing the applied pressure and the volume fraction of the glassy phase enhances the pore filling and favours the separation of grains and glassy phase during pore filling. The elimination rate of large pores is extremely reduced by an exaggerated grain growth leading simultaneously to an increased volume fraction of glassy phase in the initial porous defects.

See programme, page 32.

Fundamentals and development of fiber reinforced glasses and  
glass ceramics

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Glasses and glass ceramics usually show a low tensile and flexural strength (except pristine thin glass fibers) and a pronounced brittle fracture behaviour, which is the reason for their limited technical application. Strength-increasing effects such as thermal or chemical strengthening enhance the strength indeed, but do not influence the brittle fracture behaviour. One possible way to overcome these disadvantages is the incorporation of ceramic fibers into the glass or glass ceramic matrix. Extensively investigated so far is the unidirectional reinforcement of glasses and glass ceramics with SiC- and C-fibers. The preparation of those composites was done by a new developed sol-gel slurry method with subsequent heat pressing. The properties of the composites depend on the thermal and mechanical preparation parameters as well as on choosing the suitable components as partners. Besides the interior stresses between fiber and matrix the mechanical and chemical conditions of the interface play an important part. By this means optimisation possibilities are given with respect to high strength and good fracture toughness, which may be foreseeable sometimes leading to "tailor-made" properties, but which may be also very complex depending on the chosen system.

See programme, page 32.

FIBRE REINFORCED GLASS AND GLASS-CERAMICS BY THE SOL GEL PROCESS

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In the sixties and seventies, it was demonstrated that glass and glass-ceramic materials could be reinforced with carbon fibres and the resulting materials exhibited high strength and toughness. Slurry infiltration followed by hot-pressing remains a commonly used method for the fabrication of such composites.

Recently the sol-gel method has been applied to the fabrication of composite materials. This method has been employed in the present work to produce glass and glass-ceramic matrix materials with relatively low sintering or hot-pressing temperatures. The sol-gel technique enables good impregnation of the fibres and a uniform distribution of fibres in the composite to be obtained. Solutions prepared using metal alkoxides, metal salts, water, organic solvent and catalysts were used to infiltrate the fibres of SiC or C. Because of the very low solid yield of the solutions after gelation and drying the impregnation-drying cycle was repeated several times until the desired amount of matrix was obtained and the dried preform materials were either sintered or hot-pressed at appropriate temperatures.

The preparation of glass and glass-ceramic matrix materials, including silica, sodium borosilicate and lithium aluminosilicate compositions, and the fabrication of the composites will be discussed, and some preliminary mechanical property results presented.

See programme, page 32.

**Sintering studies of AlN for the improvement of dielectric properties  
at microwave frequencies.**

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Among the nitrogen based ceramics, AlN has a significant potential for new and demanding applications. On the one side its oxidation resistance and favourable mechanical properties make it an attractive material for high temperature applications, on the other side its favourable electrical and thermophysical properties are attractive for high performance in microelectronics.

The paper describes the work performed with a view to understanding and improving the dielectric properties of AlN. Sintering studies are described which with the addition of sintering aids such as CaO and  $\text{Ca}(\text{NO}_3)_2$  allow nearly complete densification of this predominantly covalently bonded material. A variation of the sintering parameters permits an intentional variation of the porosity as well as changes in the grain morphology.

The dielectric properties (permittivity,  $\epsilon_r'$  and loss tangent,  $\tan \delta$ ) were determined in the frequency range of 30-40 GHz. This range is relevant for the use of this material in transmission windows of radio frequency heating systems being developed for nuclear fusion reactors. It has been found that the permittivity is primarily determined by porosity. No such marked relationship with microstructural parameters can be deduced for the dielectric losses. Dielectric losses below  $20 \cdot 10^{-4}$  can only be achieved when the sintering parameters are so optimized that the initial spherical grain shape is transformed to polyhedral grains. A homogeneous distribution of the liquid phase formed by the sintering aids is essential for the close control of the dielectric losses.



See programme, page 32.

#### Fabrication and Characterization of Low-Energy Metal/AlN Interfaces

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Low-energy heterophase boundaries can be determined best by studying the equilibrium shape of precipitates in a matrix where the largest facets possess the lowest interfacial energy. Recently, fundamental studies on oxide precipitates confined in a metal matrix were performed; the precipitates were produced by internal oxidation of metal alloys /1/.

In order to create naturally grown low-energy metal/AlN interfaces pure Al and a Cu-1 at.% Al alloy, respectively have been implanted with 750 KeV  $N^+$  ions ( $1-5 \cdot 10^{17}$  ions/cm<sup>2</sup>) followed by annealing in a nitrogen atmosphere. TEM specimens with the foil normal parallel to the implanted near-surface region have been prepared by mechanical thinning followed by ion beam milling. Using conventional electron microscopy and electron diffraction studies the depth distribution, the size and the shape of the AlN precipitates as well as the crystallographic orientation relationship with respect to the metal matrix has been examined, whereby low-energy Al/AlN and Cu/AlN interfaces could be characterized. The results are compared and discussed with respect to those on naturally grown metal/oxide interfaces.

/1/ W. Mader, Z. Metallkunde (1989), in press.

See programme, page 32.

COMPATIBILITY BETWEEN TUNGSTEN AND ALUMINIUM NITRIDE :

INFLUENCE OF A CALCIUM OXIDE ADDITIVE

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In the view of cofiring multilayer ceramics for electronics, the compatibility between tungsten and aluminium nitride was studied. Aluminium nitride was chosen because of its high theoretical thermic conductivity, going with convenient electrical properties for electronic substrates, and tungsten fits with aluminium nitride for its sintering temperature and thermal expansion.

It was shown that neither bonding nor diffusion occurs between pure materials from 1500°C to 1850°C. Using calcium oxide as an additive into the metal or the ceramic, a good bonding appeared between 1500 and 1650°C when CaO was added in tungsten. Diffusion profiles of the calcium element were carried out, proving its diffusion through aluminium nitride and justifying the bonding by the formation of a calcium aluminate at the ceramic/metal interface.

See programme, page 32.

INFLUENCE OF SINTER ADDITIVES ON THE THERMAL CONDUCTIVITY OF  
PRESSURELESS SINTERED ALUMINIUM NITRIDE

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AlN powders of high purity were pressureless sintered in 1 bar nitrogen at temperatures between 2090 and 2320 K. The powders were sintered with MgO, CaO, BaO,  $Y_2O_3$ ,  $Nd_2O_3$ ,  $La_2O_3$  and  $CaO \cdot SiO_2$  as sintering additives and without additives. After sintering a residual porosity less than 2.5 % was detected by SEM. The necessary temperature for densification is determined by the formation of liquid phase containing the sintering additive, alumina and solved AlN.

Phase analysis was done by X-ray and analytical SEM.  $Al_2O_3$  containing secondary phases were detected in all material compositions. In several samples the phase distribution was additionally observed by TEM technique.

The heat conductivity predicted by a steady state method and/or by laser flash technique was measured between 18 and 148 W/(m·K) at room temperature for  $CaO \cdot SiO_2$  and CaO doped materials, respectively. The slope of the heat conductivity versus temperature dependence is relied on the kind of sintering additive. The differences between the thermal conductivity of the samples can be explained by phase composition, grain morphology of the secondary phase and influences of the additives. A numerical approach describes the influence of oxygen on the thermal conductivity of AlN ceramics.

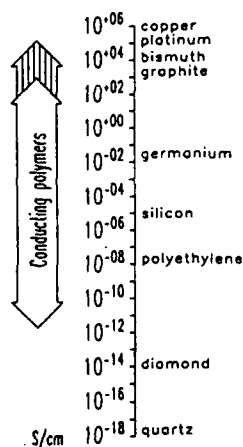
See programme, page 33.

## ELECTRICALLY CONDUCTING POLYMERS AND MOLECULAR ELECTRONICS

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A review will be given on the physical properties of conducting polymers [1], a class of materials in which recently conductivity values have been obtained which are comparable to that of copper (see Fig. 1). Using experimental data on the transient photoconductivity in polyacetylene the mobility of solitary excitations will be evaluated and various proposals of molecular electronic devices based on macromolecules with conjugated double bonds will be discussed [2,3].



**Fig. 1:** Conductivity chart: The arrow indicates the conductivity range that can be spanned by conducting polymers. The hatched area corresponds to the recent progress in polyacetylene using a novel polymerisation method [4]

### References

- [1] S. Roth, H. Bleier: *Advances in Physics* **36**, 385 (1987)
- [2] F.L. Carter (Ed.), "Molecular Electronic Devices", Marcel Dekker, New York and Basel, 1982
- [3] Proceeding of the International Conference on "Molecular Electronics - Science and Technology", Hawaii 1989, to be published by IEEE
- [4] H. Naarmann: in "Electronic Properties of Conjugated Polymers", ed. by H. Kuzmany, M. Mehring, S. Roth, Springer Series in Solid State Sciences, Heidelberg, 1987

See programme, page 33.

## High $T_c$ Superconductors for packaging

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The advantages of operating semiconductor electronics at low temperatures have been considered already for quite a long time. Recently liquid nitrogen cooled CMOS circuits have been introduced on system level in supercomputers (e.g. model ETA 10 G) improving system performance by about a factor of two due to cooling. In that same temperature range now superconducting materials become available since the advent of the "high  $T_c$  superconductors". To combine the merits of both worlds by embedding cooled CMOS circuits in superconducting high performance VLSI packaging and in superconducting shields on the same temperature level seems manageable now and might be a better choice than to "try it alone" in one or the other technique.

Keeping the silicon CMOS VLSI or ULSI chip, optimized for operation at the temperature of liquid nitrogen, taking full advantage of reduced power and electromigration and improved speed and using the superconductor "at its best" for off chip wiring and shielding is a more realistic and really interesting step forward.

The advantage of the new materials over copper or aluminum cooled to 77 K for off chip wiring at frequencies above 1 GHz will come about for wiring cross sections of the order of a few square micrometers. Improvements in speed, gate count, and integration for high performance computers will require that level of cross section perhaps not for the next two generations (designed today). But the evolution of the new materials will have to be regarded for future designs (especially as single multi chip module) getting close to the  $\mu\text{m}^2$  level where the conventional materials for wiring more and more run into limitations set by physics.

To make use of the outstanding properties of high temperature superconductors requires multi level homogeneous superconducting films of high current density, contacts, insulating dielectric films, suitable substrates on the scale of several inches and techniques for microfabrication.

From the present day status it looks likely that these requirements can be met. Single level epitaxial films on cm scale give required current densities of  $5 \cdot 10^6 \text{ Acm}^{-2}$  at 77 K, are robust and can be microfabricated down to some  $\mu\text{m}$ .

High frequency properties of such films in the range 10 to 100 GHz turned out to very interesting for technical purpose. Film preparation and high frequency properties will be reported on.

See programme, page 33.

## SILICON ON INSULATOR FOR MICROELECTRONIC DEVICES

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The interest in Silicon On Insulator (SOI) is increasing from year to year.

The development of this material is due to the better insensitivity to radiations of devices processed on SOI (rad-hard circuits). Other benefits are the increase in speed, the lower dynamic consumption and the higher packing density for Very Large Scale Integration (VLSI) applications.

Another advantage of SOI is the possibility of creating novel structures such as 3D layers or smart power devices.

To fabricate this SOI material several approaches have been used. They will be rapidly reviewed in this talk.

High dose oxygen implantation called SIMOX for Separation by Implanted OXygen is now recognized as one of the leading techniques for producing SOI material.

The formation of SIMOX structures requires two main steps : high dose oxygen implantation and annealing. The gaussian distribution of the implanted ions leads to the formation of an  $\text{SiO}_2$  buried layer surrounded by silicon containing a large density of  $\text{SiO}_2$  precipitates and crystalline defects, so annealing is required to obtain good quality SOI structures.

The first circuits reported on SIMOX were processed on material annealed at  $1150^\circ\text{C}$ . It is sufficient to form a silicon layer at the surface of the wafer in which transistors can be processed or that can be used as a seed for growth of an epitaxial layer. Nevertheless the transition region between this top silicon layer and the  $\text{SiO}_2$  buried layer still contains a very large density of defects, particularly  $\text{SiO}_2$  precipitates.

The possibility of dissolving the  $\text{SiO}_2$  precipitates and of forming abrupt  $\text{Si}/\text{SiO}_2$  interfaces was demonstrated by annealing SIMOX samples at  $1300^\circ\text{C}$  for 6 hours, and the mechanism leading to complete dissolution of the  $\text{SiO}_2$  precipitates was shown.

This talk will discuss the evolution of the SIMOX structure during annealing and describe from a thermodynamical point of view the mechanism leading to the dissolution of all the  $\text{SiO}_2$  precipitates and the segregation of the implanted oxygen to form an SOI structure with very sharp  $\text{Si}/\text{SiO}_2$  interfaces.

A review of the crystalline defects that have been observed in SIMOX will be given and the status of the material quality will be presented.

See programme, page 34.

## MICROJOINING TECHNIQUES

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Electronic components are mounted in different circuit levels. Discrete and integrated circuits are attached on carriers, on hybrid integrated circuits and on the printed circuit board level. In each level electric interconnections are made by thin and thick films. Between the levels microjoints are applied. Due to the thermo-mechanical incompatibility of the used materials semiconductors, glass and ceramics, polymers and metals the microjoints are subjected to thermal and mechanical, during the mounting and the application of the electronic systems to electrical and chemical loads.

In solid-state welded microjoints sharp crack tips cannot be avoided; time-to-fracture of wire bonds is analyzed using a constant strain limit. Soft-solder alloys exhibit a time-dependent plastic flow; the damage accumulation in uniaxial tensile samples is transferred to solder contacts at surface-mounted components. Metal-filled and non-filled adhesively bonded microcontacts are subjected to chemical degradation in a humid ambient.

New methods are discussed for manufacturing microjoints with simple and reproducible microstructures. Possible developments are the formation of high-melting intermetallics at low temperatures and the formation of conductive contacts using non-filled adhesives.

See programme, page 34.

Molecular Beam Epitaxy of HgCdTe Compounds  
for Infrared Detectors

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HgCdTe compounds are currently the most important semiconductor for infrared detection. If, today the best detectors are made on epilayers grown by liquid phase epitaxy (LPE), molecular beam epitaxy (MBE) appears the most promising. Due to its very low growth temperature (200°C) compared with LPE (480°C), it allows the growth of more sophisticated structures, such as heterojunctions and superlattices. Transmission electron microscopy on CdTe-HgTe superlattices show that the interdiffusion at each interface is less than 1 nm.

This low growth temperature allows also the use of alternative substrates, such as GaAs. Despite the large lattice mismatch between GaAs and HgCdTe, in the range of 14 %, it is possible to reduce the misfit dislocation density by using a multi-stepped composition CdZnTe buffer layer.

Different crystallographic and electric characterizations of HgCdTe MBE epilayers will be presented.



See programme, page 34.

"IBM Large Systems Packaging Evolution"

A. Oster	IBM Sindelfingen	W. Germany
G. Kleinert	IBM Entwicklungslabor	W. Germany

State of the art evolution of electronic packaging and devices can be correctly described by analyzing large systems electronic packaging architectures and their evolution with time.

Considering system cycle time and taking as main hardware parameters switching delay and propagation delay, their relative variations show the tremendous progress achieved in silicon integration.

In the late 70's major investments were made to develop and fabricate suitable packaging materials and "wiring" devices, whereas the late 80's are characterized by

- growing need for vertical integration of processor unit

and

- a decreasing differentiation between major system families.

System packaging of three major IBM system families is presented as an example.

See programme, page 35.

Applications and Properties of Polyimides in Microelectronic Devices

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Polyimides are widely used in microelectronic devices as interlevel dielectrics and  $\alpha$ -particle barriers for charge sensitive memory devices. The low thermal expansion coefficients of some polyimides and their other favourable properties, such as high temperature resistance, make them the prime material of choice for use in small scale and high integration devices (VLSI) and adhesiveless high quality flexible printed circuit boards. The most significant advantage of polyimide dielectric interlayers are their planar structure, compared with inorganic materials such as  $\text{SiO}_2$ . However, the use of polyimides has also problems such as reliability against moisture penetration and adhesive failure in general. In this talk the problem of adhesion reliability will be addressed, and examples will be given where the microscopic mechanism of adhesion has been determined by spectroscopic techniques. The results obtained on the nature of the adhesive bond in turn allow to speculate on the microscopic mechanisms for adhesive or cohesive failure of polyimide/inorganic interfaces.

Besides their use of dielectrics and  $\alpha$ -particle barriers, polyimides are also used as orienting substrates in liquid crystal displays. Examples will be discussed which suggest that the orientating effect of the polyimide substrates is due to their microscopic topography.

### Tracer Diffusion of Ag and Cu in Polyimide

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#### Abstract

Diffusion of the radiotracers Ag 110m and Cu 67 in the fully cured polyimide PMDA-ODA below and above the glass transition temperature has been investigated systematically by means of very low energy ion beam sputtering. All penetration profiles exhibit a steep Non-Fickian decay in the tracer concentration followed by a relatively flat Fickian tail. A typical example is shown in Fig. 1. The initial decay is attributed to the formation of metal clusters and is discussed in terms of Monte-Carlo simulations. The Fickian tail is related to the diffusion of single metals atoms. The Arrhenius plot of Cu in PMDA-ODA is depicted in Fig. 2. The non-linear; curvature is consistent with a free volume mechanism of diffusion.

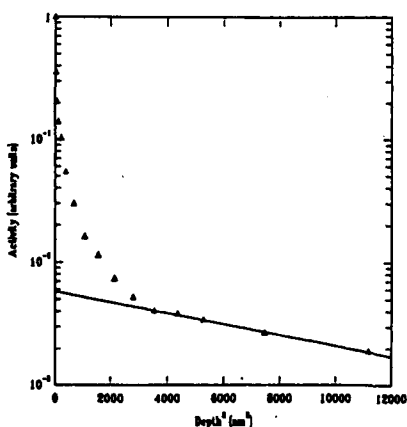


Fig. 1. Penetration profile of Cu 67 in PMDA-ODA for 69min annealing at 252 °C.

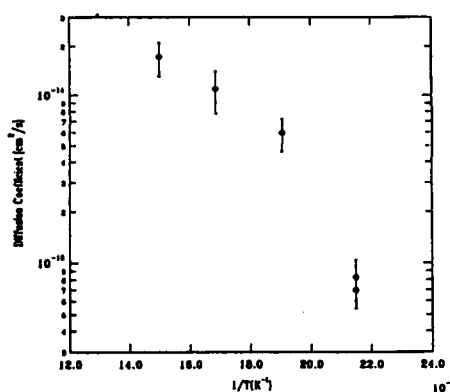


Fig. 2. Arrhenius plot for diffusion of single Cu atoms in PMDA-ODA.

See programme, page 35.

EPITAXY OF METALS ON POLYMER SUBSTRATES. T. Hoffmann, J. Petermann, Technical University Hamburg-Harburg, Polymer and Composites Group, Harburger Schlosstr. 20, 2100 Hamburg 90, W.-Germany.

Recently it has been observed that some metals form highly textured overgrowth on particular uniaxially oriented polymer films <sup>1,2</sup>. The crystallographic orientations of these polymer-metal systems are not the results of lattice matching. We suggest that the orientation relationships are due to the presence of ordered interface layers formed by chemical reactions between the metals and the polymer films.

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See programme, page 35.

# STABILITY AND REACTIVITY OF CHEMICALLY MODIFIED IRON SURFACES

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In order to investigate the structure and the reactivity of the metal-polymer interface in corresponding composites, the surface of polycrystalline iron samples has been modified in a well defined manner by organic molecules, which are attached to the metal surface by a strong chemical bond. The oxide free metal surface has been modified by S-containing molecules like mercaptanes, the oxide covered surface by silanols.

In this paper the structure of the modified surface -- according to surface analytical AES and XPS measurements -- and their reactivity -- according to electrochemical investigations -- is discussed. It is shown, that a stable chemical bond between the metal surface and the organic molecule is possible, if the reaction between both is carried out under well defined conditions. As an example, simple aliphatic mercaptanes could be bonded onto iron surfaces only, if the surface was polarized cathodically in acid electrolytes and then pulled through a second organic phase on top of the aqueous electrolyte containing the mercaptane. It will be shown, that the chemical and electrochemical reactivity of the modified surface is diminished by several orders of magnitude, yet still certain electrochemical reactions like the reduction of  $O_2$  being able to destroy the bond between the two phases. If organic molecules are attached onto oxide covered metals, then besides the stability of this bond also redox reactions inside the oxide layer must be inhibited in order to create a stable metal polymer interface.

These results will be discussed from a technological standpoint of view, the possible advantages of well prepared metal/polymer interfaces for technologically relevant composites being discussed.

See programme, page 35.

FOURIER TRANSFORM INFRARED CHARACTERIZATION  
OF THE GLASS MATRIX INTERFACE

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Fiber glass reinforced plastics improve markedly their performances when the reinforcement material has been treated with a coupling agent which directly influences the glass matrix interface properties. The most widely used coupling agents for fiber glass are silane-type chemicals.

This paper attempts to find the behaviour of these coupling agents after their application on the reinforcement surface. This study, which cannot be carried out by dispersive infrared spectrophotometry due to the obvious limitations of this technique and to the intense absorption of the infrared radiation of glass, can be satisfactorily done if non dispersive infrared spectrophotometry is used (FT-IR) and if some substractions between the spectra of fiber glass powder treated, and untreated, with various silane type coupling agents are made.

The absorption bands recorded by the above spectral subtraction clearly manifest the existence of an actual chemical bondage between glass and coupling agents and suggest a most likely polymerization of these agents when in contact with glass.

This would explain the improvement of the interfacial properties of fiber glass reinforced plastics with silane-type chemicals and, thus, the increase of performances of these composites.

See programme, page 36.

## STRUCTURE CHEMISTRY AND FRACTURE RESISTANCE OF METAL/CERAMIC INTERFACES

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The use of ceramics as structural components, as well as in chemical technology and in electronic devices is steadily increasing because of improved mechanical integrity afforded by enhanced toughness and by process control. Ceramic components must typically be connected to other materials, mainly metals. The requirements that the bonded couple must fulfill are dictated by the functions of the ceramics. However, in all cases, adequate mechanical integrity is a technical prerequisite, as reflected in the fracture resistance of the interfaces.

The fracture resistance of the interface is dictated by the adhesion which is in turn controlled by the structure, structural defects, segregants at the interface and chemical gradients developed near the interface. Structure, defects and local chemical compositions can be analyzed by different electron microscopy techniques. Frequently, chemical reactions occur at the interfaces leading either to reaction layers or to the development of chemical gradients. The structure of the interface depends sensitively on the chemical composition. The observations of interphase formation are compared to thermodynamical models.

Results will be reported wherein different metals and ceramics (predominantly oxides) are diffusion-bonded under well-defined, instrumented bonding conditions. The structure of and defects near the interface will be analyzed by different TEM techniques. Mechanical test specimens will be prepared and the crack propagation along the interface (or within one bulk component) will be studied. The fracture resistance of the interface depends on the morphology, plasticity, modulus mismatch and residual stresses. The role of the extrinsic variables will be evaluated and correlated to microstructural observations.

To fully comprehend the influence of the extrinsic effects, it is important to appreciate that debonding at metal/ceramic interfaces is a mixed mode fracture process, wherein the surfaces of the debond crack both open and shear as the debond extends. The morphology of the interface is important, because the shear component can cause asperities on the fracture surface to come into contact and thus shield the crack tip from the imposed load. Crack tip plasticity occurring in the metal is important because the associated crack tip blunting may inhibit the nucleation of a debond crack along the interface. The amount of plastic deformation near the crack tip will be measured by a quantitative evaluation of the intensity distribution of back-scattered electrons of an SEM. The influence of residual stresses on fracture resistance can be dramatic. The residual stresses aids fraction along the interface and reduces the apparent fracture energy. Residual stresses will be measured by convergent beam electron diffraction or strain contrast analysis. The microstructural results are used for an evaluation of mechanical properties.

See programme, page 36.

INTERFACE PROPERTIES OF  
ULTRA HIGH VACUUM BONDED METAL/SAPPHIRE JOINTS

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To minimize interface contamination in comparison to joints manufactured by diffusion bonding in ordinary high vacuum bonding experiments were performed in an ultra high vacuum at a pressure below  $10^{-10}$  mbar. The newly constructed apparatus allows bonding of single metal and ceramic crystals in an exact predetermined azimuthal orientation after sputter cleaning. The cleaned surfaces are in situ analysed by an Auger system.

Surface morphology of the starting and the sputter cleaned surfaces was studied by high resolution profilometry. Preorientation of the single crystals was controlled by X-ray measurements performed after the different polishing steps of the surfaces to be bonded.

Results of bonding experiments using single crystal and polycrystalline couples of Nb/Al<sub>2</sub>O<sub>3</sub>, Cu/Al<sub>2</sub>O<sub>3</sub>, and Ni/Al<sub>2</sub>O<sub>3</sub> are given. Bond strength data were obtained by measuring the fracture energy  $G_c$  and the fracture resistance  $K_c$  of interfacially notched specimens in four point bend tests. The measured fracture energy depends strongly on the bonding temperature and on the crystallographic orientation of the metal/ceramic interface. Maximum  $G_c$  values were found for the combination (110)Nb//((1120) -Al<sub>2</sub>O<sub>3</sub>, [001]Nb//[0001] -Al<sub>2</sub>O<sub>3</sub>. In conventional TEM studies no reaction layers could be detected for the couples Cu/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub>.



See programme, page 36.

BONDING OF MgO TO COPPER CONTAINING  
DILUTE ALLOY ADDITIONS\*

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There is an interest in using MgO/Cu couples for the packaging of electronic devices and the present study is designed to establish means by which strong interfaces between magnesium oxide and copper may be generated.

The bonding of magnesium oxide to copper which contained deliberate additions of manganese, cobalt or nickel has been studied by thin film deposition and by reaction bonding. Single crystal magnesium oxide and polycrystalline samples containing 3 weight percent of glass phase have been used as substrates. The influence of pressure, temperature and the atmosphere on the level of bonding have been assessed.

Mechanical property measurements of the bond strength have been made and significant bonding achieved in all cases: with the manganese-containing system showing the greatest promise.

Detailed microscopical and microanalytical studies of the bond interface have been made. These have involved the use of techniques associated with scanning electron microscopy (using both energy and wavelength dispersive X-ray microanalysis) and analytical transmission electron microscopy. In the latter case, extensive studies using especially-prepared "edge on" sample preparation have been made. Here composition profiles across the bond interface have been established using X-ray microanalysis, whilst microdiffraction (convergent beam electron diffraction) has been used to look at the state of strain at, and in the neighbourhood of, the bond interface. In the case of the manganese-containing system, a distinct reaction layer at the metal-ceramic interface has been found.

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\* This study was performed whilst the authors were in the Institute of Materials, University College Cardiff, UK.

See programme, page 36.

#### STABILITY OF METALS AND INTERMETALLICS ON GaAs

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Interface reactions between GaAs and metals are important for the formation of contacts as well as their thermochemical stability and hence the device reliability. Equilibrium phase diagrams are essential for an understanding of such interface reactions and for determination of suitable compounds which are stable in direct contact to GaAs /1, 2/. Once we know which intermetallic compound is stable it may be co-deposited as shown for  $\text{AuGa}_2$  on GaSb /3/ and for RhGa on GaAs /4/.

These metal/GaAs reactions are investigated by combining the following three approaches. First, the ternary Ga-As-M phase diagram is studied to identify possible reaction products and their mutual phase stabilities. Second, thick film diffusion couples with infinite supply of metal and GaAs are analyzed using electron microprobe and metallography to reveal actual reaction products, kinetics and morphology. Finally, these results are compared to thin film data to discover possible modifications due to thin film effects. These methods are applied to the refractory metals Mo, Ta, W and Re. Preliminary data are also presented for Ti, V, Cr and Si on GaAs. These data are compared to results on Co/GaAs from Chang's group /5, 6/.

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See programme, page 37.

Effects of Brazing Parameters on The Microstructures and Thermal Fatigue Behaviour of The AlN/Cu Joints Produced by An Activated Ag-Cu Filler Material

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Thermal design is one of the key issues with power chips used e.g. in smart power units. Dissipation power density over 5 W/cm<sup>2</sup> makes it important to reduce internal thermal resistance of packaging. The metal heat spreaders, such as copper, are used to extend interface between semiconductor chip and substrate. Furthermore, high thermal conductive ceramics substrate will reduce temperature distribution and hot spots in assembly.

The advantages of aluminiumnitride over beryllia are its nontoxicity and lower coefficient of thermal expansion (close to the CTE of silicon), while as compared with silicon carbide the advantages are lower propagation delay of signals and higher chemical stability. Eutectic bonding of Cu-CuO to the Al<sub>2</sub>O<sub>3</sub>-layer (30-50 µm) formed on the surface of AlN has been produced commercially, even though there still are adhesion problems.

In this study we have used Ti-activated Ag-Cu-based brazing alloys to join copper foils to AlN-substrate at temperatures which are considerably lower than those used, for example, in eutectic Cu-CuO bonding. Decreased joining temperatures reduce also thermal stresses of bonded layers generated by large difference between the thermal expansion coefficients of the materials to be bonded.

Copper foils were brazed to AlN with eutectic Ag-Cu filler material being either alloyed with Ti, coated with Ti by vacuum evaporation or activated by a thin Ti-interlayer between the braze alloy and copper metal. Joining was carried out in a high vacuum furnace at temperatures 750, 800, 820 and 850 °C. Good quality joints were obtained when brazing temperature is 800 °C or higher and cooling rates less than about 2 °C/min. Other heating and cooling procedures where cooling rate was altered considerably with temperature were also found feasible.

The brazed joints were tested structurally before and after thermal cycling. The microstructures and constitutions of the brazes were studied optically and with the SEM/EPMA technique. In all the joints studied relatively high concentrations of titanium at the interface between the braze alloy and the nitride was found to produce good spreading of the filler materials as well as strong bonding of copper to AlN.

See programme, page 37.

GLASS-CERAMIC COATINGS ON HIGH  
TEMPERATURE ALLOYS

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The chemical reactivity of alloy surfaces at high (or low) temperatures can be controlled by surface treatment. One technique is to coat the surface with glass-ceramics - materials which can be tailored, by means of composition and thermal history, to have desired values of selected properties such as refractoriness, thermal expansion, impermeability etc. A good coating must be well bonded to the substrate. This necessitates a thermal expansion (TCE) match between the coating and the alloy and a strong chemical bond. We report our work on coating titanium and nimonic alloy with TCE matched lithium silicate based glass-ceramics and the importance of the degree of oxidation at the interface.

In the case of coating of non-preoxidised nimonic, a reaction occurs in which chromium is oxidised by phosphate in the glass to give  $\text{CrO}$  and  $\text{Cr}_2\text{P}$ . The consequent depletion of  $\text{P}_2\text{O}_5$ , the nucleating agent, in the region of the interface leads to a coarse microstructure in the glass-ceramic. Chromium dissolves into the glass during coating as  $\text{Cr}^{2+}$  and diffuses rapidly such that, at extended coating firing times, it has diffused as far as the coating surface where it is oxidised to  $\text{Cr}^{3+}$ . This species has a lower solubility than  $\text{Cr}^{2+}$  and a crystalline phase  $\text{LiCr}(\text{SiO}_3)_2$  precipitates.

Where preoxidation is carried out, an oxide layer is formed on the nimonic which is readily wetted by the glass. This oxide layer prevents direct reaction between chromium and the glass constituents. The oxide layer is  $\text{Cr}_2\text{O}_3$  i.e.  $\text{Cr}^{3+}$  is present and, since its solubility and diffusivity are low,  $\text{LiCr}(\text{SiO}_3)_2$  is now precipitated at the oxide/glass interface. Phosphate is no longer reduced and the development of the desired coating microstructure is unhindered.

In the case of titanium without a preoxidised surface, the redox reaction is between Ti and the silicate component in the glass giving  $\text{Ti}_5\text{Si}_3$  and oxygen at the interface, leading to foaming of the glass. Preoxidation to give a  $\text{TiO}_2$  layer reduces this effect but the oxide is only weakly adherent to the metal thus giving poor coating strength. Addition of adherence oxides e.g.  $\text{CoO}$  produces an alternative reaction to give  $\text{TiO}_2$  and Co. This results in improved wetting of Ti by the glass and better coating adhesion.

See programme, page 37.

Authors

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Title

Active metal brazing of silicon nitride

Active metal brazing of oxide ceramics especially  $ZrO_2$  and  $Al_2O_3$  is well established. For applications where high wear resistance and low specific weight is required, for example a rocker arm equipped with a ceramic plate, silicon nitride is one of the most promising ceramic materials.

In this paper newly developed Ti-containing active metal brazes will be presented. The interfacial reactions between active metal brazes and ceramic have been investigated by microprobe analysis and diffraction methods. The results of strength tests of active metal brazed  $Si_3N_4$ /mild steel-joints and the influence of Ti-content on the strength and wetting behaviour will be discussed.

Besides a high strength of the brazed joints one aim is to minimize the residual stresses in the joint. Due to the low coefficient of thermal expansion of  $Si_3N_4$  the mismatch between silicon nitride and metal generally will be higher than the mismatch between  $Al_2O_3$  or  $ZrO_2$  and metals. This leads to higher thermal stresses in  $Si_3N_4$ /metal-joints. These stresses can be reduced by choosing metals with low coefficients of thermal expansion or by a high ductility of the filler metal and by proper design of the interfaces and the geometry of the specimens or components.

This has been verified by measurements of the elastic deformation of the specimen which is an approximation for the amount of residual stresses. The results will be compared with stress measurements carried out by X-ray-diffraction.

It can be shown that the choice of the suitable filler metal can reduce thermal stresses considerably and thus can produce reliable  $Si_3N_4$ -to-metal-joints.

See programme, page 37.

The metallization of AlN by a W-containing paste.

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The bonding of Ni to AlN by the metallization of AlN and by brazing, has been investigated. The interfacial reactions that take place during the metallization, have been studied. For that, cross-sections of the bonds were analysed by SEM and EDAX. Before metallization the ceramic parts have been cleaned by firing. The atmosphere and the temperature during such firings have been varied. Influences of these firing conditions, and of the atmosphere during the metallization will be discussed. In view of the bonding to nickel, the possibilities to braze the thus formed metallization layers by various braze materials will be touched on.

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Titel : Thermal stability of SiC-fibre reinforced  
Ti6Al4V-alloys

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Abstract : For the application of SiC-fibre reinforced Ti6Al4V-alloys at temperatures up to approximately 500°C investigations of thermomechanical properties and of the stability of the fibre-matrix interface were performed. The composites were processed using SiC-fibres coated with a carbon rich SiC-layer (AVCO) by hot isostatic pressing. Using this technique, materials with a fibre volume fraction of 40% can be obtained. The samples were tested at temperatures up to 600°C. For the study of the interfacial stability the composites were annealed in vacuum at 600°C between 1 and 100 hours. The structure and composition of the interface was investigated using analytical transmission electron microscopy and Auger electron spectroscopy.

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The Fibre-Matrix Interface in Cast  $\text{Al}_2\text{O}_3$ -Aluminium Alloy Composites

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The basic idea of fibre reinforcement is to enhance strength and stiffness of common materials by adding strong and high modulus fibres. Therefore external loading has to be transferred from the matrix material to the fibres and vice versa requiring a good bonding between fibres and matrix. To make a good composite therefore tailoring and controlling the fibre-matrix interface is of great importance.

The present investigation deals with fibre-matrix interfaces in cast  $\text{Al}_2\text{O}_3$ -AlSi-base alloy composites produced by squeeze casting methods. Several surface and microanalytical methods (scanning electron microscopy, Auger electron spectroscopy, X-ray photoelectron spectroscopy and analytical transmission electron microscopy) have been used to study the interface [1,2].

Most of the fibres in a  $\text{Al}_2\text{O}_3$ -AlSi12CuMgNi composite show a reaction layer between fibre and Al-matrix. The thickness of the interface lies between a few and several hundred nanometers depending on fibre type, production conditions, heat treatments, local fibre surface condition and local alloy composition. Mg-enrichments are detected in the interface phase. Fracture analyses show a strong bonding between fibre and matrix giving excellent improving of the mechanical properties of AlSi12CuMgNi by the fibre reinforcement.

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European Congress on Electron Microscopy, York, 1988

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Fresenius Z. Anal. Chemie



See programme, page 38.

NEW TEM TECHNIQUES FOR THE CHARACTERISATION OF A BOUNDARY; W.M. Stobbs,  
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It is only too easy to fall into the trap of believing that the TEM images which can so often be obtained at "atomic" resolution of irregular steps at interfaces can have unequivocal interpretation given a conventional modern approach to the simulation of the detailed changes to be expected as a function of specimen thickness and objective defocus. The reasons why this is rarely true will be discussed and the information which can be reliably obtained from such images delineated. Not least amongst the problems is the fact that for even a weak phase object there is a tendency for local variations in spacing to be smeared out in the image while this is precisely the effect of most of the more commonly used "image filtering" techniques which allow a micrograph to be obtained which can more readily be compared with the simulation. When it is then remembered that the relaxation process, which it is usually the purpose of the investigation to study, will also tend to even out local variations in spacing it is hardly surprising that "matches" are not infrequent; it is only their reliability which is questionable. If the solution of the local variation problem remains difficult several other characteristics of a boundary, such as its rigid body displacement, can readily be inferred from the fairly naive interpretation of good high resolution images.

Currently, and mainly because of uncertainties in the interpretation of the effects of energy loss on an image, the "evasion" of the problems of high resolution is not without its attractions. Accordingly the alternative TEM techniques which can be used to find out about the structure and composition of a boundary will be described and their respective uses exemplified. In this context the weak beam method still has a great deal of potential and examples of its use will be given. Finally the uses of the newly developed Fresnel method in the area of the characterisation of interfaces generally will be noted. It can be of considerable value in the evaluation of boundary roughness and segregation and the method has, for example, been applied to problems as diverse as the evaluation of the roughness of AlGaAs/GaAs multilayers and the characterisation of the compositional grading at the Si/SiO<sub>2</sub> interface. Recently the method has also started to be applied to the evaluation of the interface potential at well characterised semiconductor/metallic phase boundaries but here the interpretation is undoubtedly still questionable.

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#### GRAIN BOUNDARY ENGINEERING

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It is well accepted that a basket of mechanical properties (e.g. strength) may be controlled through alterations to the grain size. Hence grain size becomes a key parameter in the materials selection routine and using a materials processing route to refine or coarsen the grain size of a crystalline engineering material is accepted practice. In many cases the processing is of a thermomechanical nature and controlling the processes of recrystallisation and grain growth is then central to the thinking.

Grain boundary engineering incorporates the idea of specifying and achieving a particular grain size distribution through a processing procedure. However, it also incorporates the idea that grain boundaries with different geometries may well have different properties. This essentially means that boundaries at or near to "special" geometries (i.e. high density coincidence site lattice configurations) may have properties different from those which may be thought of as "random". Much remains to be done on the quantification of property/geometry relationships of this type.

This paper is primarily concerned with the effect which subtle alternations in the processing may have on the distribution of boundary geometries. The local grain boundary geometries have been determined using microdiffraction in an analytical electron microscope and the diffraction mode available through the use of electron back scattering in a scanning electron microscope. These techniques have been adopted to investigate local textural changes (termed the grain misorientation texture) which accompany both recrystallisation and grain growth in engineering alloys. Amongst factors which will be discussed include the measurement of local strain and the mechanisms by which migrating grain boundaries interact with precipitate dispersions. Some insight into the transition between normal and anomalous grain growth is given.

See programme, page 38.

#### REACTIVE DIFFUSION

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Under the heading "Reactive Diffusion" are described all the diffusive processes between materials which lead to the formation of intermediate phases (coatings, sintering, oxidation, silicidation...).

The prediction of the nature of these phases, of the various times when they appear (induction period), of their kinetic growth law,... remains as yet not possible. These inadequacies have several origins : one has to face with i) a non equilibrium state and ii) a not purely diffusive state. Processes at the interfaces play a key role, so that the growth kinetics may be diffusion controlled or/and interface controlled, which leads to linear, parabolic or more complex growth laws. The time or space sequence of the new phases is governed by kinetic relations, which depend on several diffusivities and (poorly known) rate constants, as well as by the geometry of the specimen.

Some simple arguments allow to rationalize qualitatively the course of the events, as long as one species is more mobile than the other one, a situation not exceptional in intermetallics, and the generated internal stresses remain at a negligible level. Competitive growth of two or three compounds will be discussed on these bases.

See programme, page 38.

Thermodynamic and Kinetic Considerations of the Ti-Si  
Diffusion Couple

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Metal silicides are used as refractory and electronic materials due to their high thermal and chemical stability and good electrical conductivity. Transition metal silicides, and  $\text{TiSi}_2$  in particular, have already been proved to be useful in microcircuits as a contact material. A less useful property of titanium silicides is their brittleness, which can give rise to problems in titanium-matrix composites or when joining titanium to silicon-based ceramics.

In addition to  $\text{TiSi}_2$  there are four other silicides in the Ti-Si system, namely  $\text{TiSi}$ ,  $\text{Ti}_3\text{Si}_4$ ,  $\text{Ti}_5\text{Si}_3$  and  $\text{Ti}_3\text{Si}$ , which have been much less investigated. Particularly this is true for the  $\text{Ti}_3\text{Si}$  compound, and therefore, a special interest has been given to this phase.

The existence of stable (or metastable) phases as well as their relative positions in a diffusion couple can be seen from the phase diagram determined either experimentally or, if reliable thermodynamical data are available, calculated by one of the computer programs such as the Thermo-Calc. In present work the Ti-Si phase diagram has been assessed by using the latest experimental phase diagram and the available thermodynamical data.

For kinetic considerations diffusion couples were prepared from the p-type silicon single crystal wafers and titanium of commercial (C.P, grade 1) and high purity (H.P, 99.99+). The diffusion couples were annealed at  $1100^\circ\text{C}$  for different periods of time, up to 100 hour, in a high vacuum furnace. The samples were examined by utilizing SEM/EPMA technique.  $\text{TiSi}_2$  and  $\text{TiSi}$  are the two fastest growing silicides, while  $\text{Ti}_3\text{Si}_4$  and  $\text{Ti}_5\text{Si}_3$  layers remain relatively thin. The results obtained with C.P Ti and H.P Ti indicate that the impurity contamination has a great effect on the stability of  $\text{Ti}_3\text{Si}$ .

The rate of growth and interface migration of the silicides were also simulated with a computer using a diffusion couple model of planar interfaces. In these calculations the movement of each silicide layer has been simulated with a mass balance equation; one for each interface. The calculated thicknesses of the fastest growing  $\text{TiSi}_2$  and  $\text{TiSi}$  silicides correspond quit well to the results of experimental measurements.

See programme, page 39.

Interfacial Reactions and Amorphous Phase Formation in Ni-Zr Composite Wires

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The progress of solid-state reaction in composite Ni-Zr wires with different elemental layer thicknesses has been studied in detail. The samples were prepared from 25  $\mu\text{m}$  thick elemental Ni and Zr foils by a foil winding technique and by codeformation using swaging and wire drawing. X-ray diffraction, differential scanning calorimetry, magnetization and resistivity measurements and transmission electron microscopy (TEM) were used to monitor the reaction during constant rate heating and to characterize the different reaction products. For kinetic reasons, an amorphous phase initially forms at the interface between the elemental layers. As soon as the layer thickness exceeds a critical value, the intermetallic NiZr phase appears at the interface between the amorphous phase and pure zirconium as shown by the TEM investigations. This is due to a reduced velocity of the reaction front caused by the longer diffusion path which enables the intermetallic phase to become stable. Therefore, crystalline NiZr grows until all zirconium is consumed. This leads to a two-phase material of the amorphous phase and intermetallic NiZr that remains unchanged until crystallization of the amorphous  $\text{Ni}_{68}\text{Zr}_{32}$  sets in. In order to obtain a fully amorphous material, the interdiffusion reaction must be completed (or especially the Zr layers must be completely reacted) before the intermetallic phase starts to form. This is achieved for composites with about 100 nm thick elemental layers, resulting in bulk amorphous material.

See programme, page 39.

Phase Sequence in the Solid State Amorphization Reaction of  
Metallic Thin Films

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The solid state amorphization reaction of thin metallic multilayers is reviewed in the view of competing time scales. Providing a thermodynamic situation for a solid state reaction by choosing the suitable constituents it is shown that a Zr-Co diffusion couple forms first an amorphous interlayer and as a second product the intermetallic compound ZrCo. For the Zr-Al system the results show in contrast that the easy formation of an intermetallic compound prohibits the amorphous phase formation in a simple annealing experiment. Slight irradiation during the solid state reaction seems to increase the nucleation barrier for the compound formation and favours the amorphization process. The crystal to glass transition is compared to ordinary melting and limits of the stability range of crystalline structures are discussed in the light of results obtained by coevaporation of binary systems at high substrate temperatures.

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Some aspects of the metal-metal bonding.

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This talk will present the results of a study concerning a metal-metal bonding technique used to make automotive multimaterial component e.g. piston or suspension arm. The reliability of the interface bonding is directly related to the process parameters by the classical well-known scheme :

process parameters  $\leftrightarrow$  microstructure  $\leftrightarrow$  mechanical characteristics

In this paper, we examine what are the main parameters in a metal-metal bonding realized by inserting an electroplated Ni-resist piece in an aluminium cast alloy using squeeze casting. Four kinds of plating were tested in different conditions of inserting.

In order to assess the intrinsic mechanical characteristics of the interface bonding, we compare the results of Finite Element Method calculations on metal-metal interfaces with the experimental results ; then we examine the effects of the squeeze casting pressure, the pouring temperature and the insert temperature on the bonding strength.

This study is illustrated with an industrial application.

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#### ADVANCED TECHNOLOGY TITANIUM CARBIDE COATED BEARINGS

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Conventional oil/grease lubricants are no longer sufficient to solve complex space-age tribology problems encountered in aerospace applications, as well as in other extreme environments. To provide such critical mechanisms with the necessary reliability and long life, it is mandatory to make use of advanced materials and/or special solid lubricants, which in most cases are applied as coatings. Nowadays, there are many different types of solid lubricants available, both organic and inorganic. Each specific solid lubricant is adapted to a special mechanical function or/and operating environment. Inorganic solid lubricants can be soft metallic such as Ag, Au and Pb, soft non-metallic such as  $\text{MoS}_2$ , BN and graphite, and hard non-metallic.

This presentation is concerned with the latter type of solid lubricants, more precisely, with hard, wear-resistant, ceramic-type titanium carbide (TiC).

TiC (typical microhardness: 35000 N/mm<sup>2</sup>) is deposited by means of chemical vapor deposition (CVD) techniques on metallic components subjected to stationary, vibrating, rolling or sliding tribo-contacts in extreme environments. CVD is a process which takes place at 900-1000° C for several hours. Because of this only substrates, which support such a thermal load, are considered. A good metallurgical bond is created between the TiC coating and the substrate.

These coatings can be extremely beneficial when used alone, but also combined with conventional oil/grease lubricants, or with not conventional solid lubricants.

TiC coatings, which are since many years used to extend the lifetime of cutting - and metalworking tools, have been used more recently, with spectacular success in ball bearings and fretting joints, especially in the aerospace industry. High precision TiC-coated steel balls are used in conventional steel ball bearings to upgrade them, making them compatible with very demanding environments and operating conditions. In addition, the extraordinary tribological properties of TiC make it a very attractive coating material to protect mechanically active surfaces other than in ball bearings. TiC coatings are excellent diffusion barriers and are therefore frequently used to prevent cold welding and fretting damage in highly stressed stationary vibrating contacts, in hold down and release mechanisms and latches on deployables on board spacecraft.

The paper will briefly review how TiC coatings are obtained, what the particular properties are of TiC-coated components, and why they perform well.

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Keynote

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Local Experiments with the Scanning Tunneling Microscope

The abstract of this  
paper was not available at the  
time of printing.

See programme, page 40.

#### **A Scanning Tunneling Microscope for the examination of local material faults**

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For the better understanding of local material faults like dislocations, grain boundaries, and cracks the stress and strain field around these effects must be known in a range where continuum theories predict singular behavior. In addition, the knowledge of atomic positions near dislocation cores or at the tip of cleavage cracks are needed to test computer simulations and to understand impurity segregation near defects.

The extremely high resolution of a Scanning Tunneling Microscope allows to examine these defects in detail; but it is difficult to locate local faults like a crack tip or a dislocation core if the defects are not numerous. To find these locations it is necessary to work with the STM on a large surface area, usually much larger than can be scanned with the fine drive. Therefore a special three dimensional coarse drive was designed. The drive consists of three single inertia drives. Ruby spheres glide on sapphire plates to reduce friction. The plates are notched to force each drive to move in a given direction; because of the low friction of this system a special construction for vertical positioning was built. The three dimensional coarse drive can be used to obtain an overview of the surface. It scans a volume of 20 mm x 20 mm x 3 mm with an adjustable single step resolution between 0.1 and 1.0  $\mu\text{m}$ . Because of the high step accuracy of the coarse drive computer controlling of the coarse drive and the fine drive allows the examination of macroscopic specimens with a resolution of up to 200 nm and allows to follow cracks up to their tip. The macroscopic topographic picture can be examined on the graphic screen with a resolution of 200 nm in order to detect grain boundaries, particles or cracks. Special features can be chosen and since all coordinates are stored in the computer, areas of interest can be examined with a higher magnification in normal STM-modes.

The construction of the coarse drive, algorithms for searching and following local defects and first examinations of local material faults like dislocations and slip bands will be shown. The current efforts concentrate on the examination of crack tips in brittle materials. The future aim of the study is to measure the local lattice distortions near crack tips with the STM and to compare the results with atomistic calculations.

See programme, page 40.

A Fully Automated, "Thimble Size" Scanning Tunneling Microscope.

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A novel, fully automated, high-stability, high-eigenfrequency Scanning Tunneling Microscope (STM) has been developed. Its key design feature is the application of two piezoelectric ceramic tubes; one for the x-y-z motion of the tip, and one for a vertical piezo motor used for coarse positioning of the tip relative to the specimen. By means of the linear piezo motor the tip can be advanced in steps between 160 nm and 0.2 nm. The walking distance is >2 mm with a speed of 30 steps/sec. The piezo motor positioning implies that this STM is fully controlled by electronic means and no mechanical couplings are needed. The axial symmetric construction is rigid, small and temperature compensated, yielding reduced sensitivity to mechanical and acoustic vibrations and temperature variations. The sample is simply placed on a piece of invar, which surrounds the scanner tube and the piezo motor, and is held by the gravity only. This allows for easy sample mounting. The sensitivity for the z-movement has been calibrated using a laser-beat frequency-interferometry method. The performance of the microscope will be demonstrated showing atomic resolution on Si, the polishing procedure (surface roughness) of Cu and Mo, and imaging the helix structure of doublestranded native DNA.

See programme, page 40.

### **Theoretical Study of Scanning Tunnelling Microscope Images of Graphite**

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The surface of graphite has been widely studied with the scanning tunnelling microscope (STM). A number of these studies have found that the STM image of this surface is characterised by giant corrugations ranging in magnitude from 1 Å to 10 Å. Some studies have reported corrugation amplitudes that are even larger than this. Using Tersoff and Hamann's<sup>1</sup> model of the STM, Tersoff carried out a study of the STM image expected from a graphite surface<sup>2</sup>. He found that the giant corrugations observed experimentally on the surface of graphite could be explained in terms of the electronic structure of graphite. Tersoff and Hamann's model includes only tunnelling to the s wavefunction of the STM tip. In this study the effects of tunnelling to the p wavefunctions of the tip will be investigated.

When tunnelling to the p wavefunctions of the tip is included it is found that the magnitude of the corrugations expected in an STM image of a graphite surface is considerably reduced from the value predicted with the s wave only model. The large reduction of the corrugation amplitude arises because the magnitudes of the tunnel currents to the  $p_x$  and  $p_y$  orbitals are of the same order of magnitude as the currents to the s and  $p_z$  orbitals even though the  $p_x$  and  $p_y$  orbitals have nodes directed towards the surface. This is a surprising result as the  $p_x$  and  $p_y$  states are generally considered to make an insignificant contribution to the tunnel current. The results of this study provide further evidence that the anomalously large corrugations observed in STM images of graphite are caused by contact between the tip and the surface<sup>3</sup>.

A discussion of the effects of the p wavefunctions of the tip on the resolution of the STM of a number of other surfaces will be presented. It will be shown that the effects of including p states in the STM tip electronic structure has a number of important implications for interpreting STM Images.

#### **References.**

1. J. Tersoff and D.R. Hamann, *Phys.Rev.B* **31** 805 (1985).
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3. J.B. Pethica, *Phys.Rev.Lett.* **57** 3235 (1986).

See programme, page 41.

### Scanning Tunneling Microscopy of Macromolecules.

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There is increasing interest in the application of STM to the imaging of macromolecules such as proteins, DNA and Langmuir-Blodgett films. Although there are an abundance of images of such molecules, image interpretation is in many cases difficult since the contrast mechanisms can vary from molecule to molecule. The possible mechanisms giving rise to contrast in STM images of molecules will be discussed along with the use of spectroscopic techniques which can give insight into the nature of the image. For example, spectroscopy can reveal cases where the tip of the STM is in contact with the molecule during imaging, whether the molecule is conducting and has either localised or extended states, and whether there is an image dipole interaction between the molecule and substrate.

See programme, page 41.

## **FORCE MICROSCOPY IN MATERIALS SCIENCE**

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The STM (Scanning Tunneling Microscope) has developed to a powerful tool in surface science. However, this method is restricted to electrically conducting surfaces. This limitation is overcome in AFM (Atomic Force Microscopy) which is also suitable to study the topography of insulating surfaces on an atomic scale. In this technique a tiny force sensor is raster scanned across the surfaces and probes the interaction forces (interatomic, frictional, magnetic, electrostatic, etc.) between sample and sensor tip. Recent contributions of AFM to topographic imaging and to measuring forces on an atomic scale are reported. Results on layered materials, such as graphite and CDW materials, and on vitreous silica show the potential of high resolution. Special emphasis is given to measurements on silver halide monocrystals and on hydrogenated amorphous carbon ( $\alpha$ -C:H) layers. On different AgBr crystal faces characteristic differences were found which help to understand distinct properties of these surfaces in photographic emulsion technology. AFM measurements on different  $\alpha$ -C:H films showed a clear correlation of topography and tribological properties such as friction and wear. Both applications show the potential of this new technique in the field of materials science.

See programme, page 41.

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## Construction of an Atomic Force Microscope and Application in Surface Chemistry

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Since the introduction of atomic force microscopy in 1986 by Binnig, Quate, and Gerber there has been a rapid development in construction and application. The atomic force microscope (AFM) scans the surface and measures the forces between the surface and a tip. The tip is mounted on a flexible cantilever with a spring constant typically between 1 and 100 N/m. The deflection of this cantilever is detected by a scanning tunneling microscope (STM), in some cases by optical methods or capacitive methods.

A critical point of AFM devices with STM detection is the adjustment between lever and STM tip. A simple force detection arrangement, which allows use of a conventional STM as force detector, has been developed by Bryant, Miller, and Yang. In a further simplification we propose a force detector which measures the deflection of a thin metal membrane covering an insulated STM tip.

AFM and STM are a useful tools in surface chemistry. Single organic molecules on a surface can be made visible. STM in air and solution are shown and application of AFM in surface chemistry is discussed.

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See programme, page 41.

#### Work Function Raster Microscopy

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Combined Auger and work function measurements deliver microscopic correlations between the structural, chemical and electronic properties of a solid surface and the local elemental composition. Such measurements can be performed with the cylindrical mirror analyser (CMA) of a scanning Auger microprobe (SAM) to identify Auger electrons as well as the onset energy of secondary electron emission. The shift of this onset energy is a direct measure of local work function changes  $\Delta\phi$ . Using a feedback loop to maintain a constant surface potential, variations of the work function can be displayed directly during rastering the primary electron beam across the sample surface. Corresponding studies have been performed for sputter generated tapered sections of Ni-Cr multilayer systems, and at polycrystalline Al surfaces. It is found that  $\Delta\phi$ -investigations enable the characterization of structural and chemical surface states, the latter even below the detection limit of AES. In the present measurements local work function changes are detected with a resolution of 10 meV.

Work function microscopy utilizes in principle all secondary electrons instead of the small number of Auger electrons. Hence, a higher lateral resolution compared to scanning Auger microscopy is achieved because of the possible reduction of the primary beam current.

Such potentialities of work function raster microscopy are demonstrated e.g. by comparing the structure of a small impurity particle in the Ni-Cr multilayer system as obtained with work function spectroscopy, Auger electron spectroscopy and raster electron microscopy.



See programme, page 42.

### How sensitive is acoustic microscopy?

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The applications of acoustic microscopy in the study of materials are growing rapidly. This is not because of resolution alone, but rather because of the unique contrast from the interaction of the acoustic waves with the elastic features of the specimen<sup>1</sup>. In high modulus materials, including almost all ceramics, most semiconductors, and many metals and alloys, Rayleigh waves are excited in the surface. By adjusting the defocus, the contrast can be made extremely sensitive to features that affect the propagation of Rayleigh waves. A simple example is the imaging of grain structure in a polycrystalline material. It is necessary to polish the specimen to a high standard of flatness, because otherwise the defocus would vary over the specimen and the resulting contrast might swamp the contrast from elastic variations. But it is not necessary to etch the specimen, indeed it is preferable not to, because the grain structure is revealed by the variation of surface wave velocities from one grain orientation to another. Measurements of surface wave velocities as a function of orientation can be made using a cylindrical, or line-focus-beam, lens<sup>2</sup>. This technique enables an estimate of the smallest change in elastic properties that can be detected by acoustic microscopy to be made. The acoustic microscope also has great sensitivity to surface cracks. Again this arises because of the effect on Rayleigh wave propagation. For some time the question has been asked: "how fine a crack can you detect with the acoustic microscope?" There are good theoretical grounds for supposing that there is no limit to how fine a crack can be, and still scatter Rayleigh waves. There is now increasing experimental evidence that indeed the acoustic microscope can detect the finest of cracks, provided that atomic contact has been broken between the two faces. This comes partly from comparative studies with light microscopy and scanning electron microscopy; and partly from studying Rayleigh wave interference fringes associated with cracks. Both of these indicate that so far from the contrast getting weaker as the crack faces come closer together, the contrast extends undiminished right to the tip, and that the tip is itself an acoustically well defined feature.

1. *An introduction to scanning acoustic microscopy*. Andrew Briggs, Oxford University Press (1985).
2. *Material characterization by line-focus-beam acoustic microscope*. Junichi Kushibiki and Noriyoshi Chubachi, IEEE Trans. SU-32, 189-212 (1985).

See programme, page 42.

Reflective Scanning Acoustic Microscopy for  
Imaging Sub-Surface Structures  
in Solid State Materials

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The scanning acoustic microscope provides the non-destructive examination of hidden subsurface structures in solid state material, suitable for the inspection of coated parts. Techniques for obtaining a defined characterization of the interfacial microstructure of layered composites are demonstrated.

The calibration conditions for the detection of hidden structures are evaluated by means of  $V(z)$ -characteristics which indicate the acoustic response signal and therefor the contrast conditions in selected depths, dependent on the frequency, coupling fluid and material consistence. By measuring defined test samples, the indepth imaging positions concerning the focusing limits are estimated. The feasibility for resolving structural defects below the surface and characteristics of microstructures, especially of hard layers, is discussed.

See programme, page 42.

Direct Measurements of the SAW Velocity and Attenuation  
Using Continuous Wave Reflection Scanning Acoustic Microscope  
(SAMCRUW)

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Conventional acoustic microscopes using pulse echo technique are able to perform high resolution images by x-y scanning of the surface of a sample, or to measure locally the surface acoustic wave (SAW) velocity using the  $V(z)$  curve, obtained by scanning the distance  $z$  between the lens and the sample. But the interpretation of the contrast of an image is often very difficult. There are several sources of contrast (direct reflection, SAW propagation, topography of the sample, etc.), and these microscopes are measuring the amplitude of the surface echo, but cannot generally measure the phase, which is of great importance for the interpretation of the contrast.

An acoustic microscope using continuous waves (CW) has been developed on the basis of a network analyzer. It is able to measure the amplitude and the phase of the scattering parameter  $s_{11}$  (reflectance of the lens + sample), from which important informations for the interpretation of the image contrast are obtained. It allows also to perform quantitative measurements of local velocity and attenuation changes of the SAW, by measuring  $s_{11}$  as a function of :

- the frequency  $f$  of the ultrasounds. Pulse echo response can be calculated by FFT, with a time domain resolution sufficient to separate the direct and SAW reflections (equivalent short pulse spectroscopy).
- the height  $z$  of the lens. Velocity and attenuation changes of the SAW are directly obtained by FFT (CW  $V(z)$  curve).

Some applications of this technique to the study of surface and layers will be presented.

See programme, page 42.

Use of scanning acoustic microscopy to characterize cathodic arc deposited CrN films

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It will be reported about the results of non-destructive testing of cathodic arc deposited films by using scanning acoustic microscopy. For the characterization of CrN-coatings it is necessary to know the distribution, site and size of inhomogenities like droplets and other within the film.

The advantage of this technique is the penetration into the film in the manner and the high accuracy in the characterization of the defects with a resolution in the range of better than 1  $\mu\text{m}$ .

Based on depth profile measurements the position and the size, particularly the expansion in z-direction is possible to be determined.

Furthermore irregularities in the transition zone substrate/coating are found and the film thickness is measured by  $v(z)$ -curves.

In the presentation the results of the measurements carried out will be discussed in detail. Furthermore the potential of a successful application of the scanning acoustic microscopy in the non-destructive testing of thin solid films will be demonstrated.

See programme, page 42.

**Investigations on the Defocussing Effects in a SAM at Straight  
Amplitude and Phase Edges.**

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It will be shown that the optical transfer-function of a scanning acoustic microscope (SAM) is described essentially by an incoherent point to point representation if the focus is situated on the sample surface.

With an increasing defocus the effect of coherent single point imaging becomes more impressive, as the spot on the sample is blurred onto a larger area. The  $V(z)$ -contrast is overlayed to both of these effects.

The amounts of the contrasts described by the incoherent OTF, by the coherent OTF, and by the  $V(z)$ -function will be shown qualitatively at a simple structured object.

Furthermore we try to show quantitatively where the parts of the contrast in the images came from.

## POSTER PRESENTATIONS

Melt Refining, Casting Technology and Cast Iron

Preparation and Processing of Powders

Surface Treatments and Laser Processing

Fundamental Aspects of Superalloys

Single Crystal Superalloys

Microstructure and Properties of Superalloys

Heat Resistant and High Strength Steels

High Temperature Intermetallics

Phase Diagrams for High Temperature Materials

High Temperature Corrosion and Oxidation

Ceramics and Non-Metal Composites

High Temperature Superconductors

Light Alloys and Light Metal Matrix Composites

Rapidly Solidified and Amorphous Metals

Shape Memory Alloys

Electrodeposited Layers

Biomaterials

Metal/Non-Metal Interfaces and Reactions

Metal/Metal Reactions and Wetting

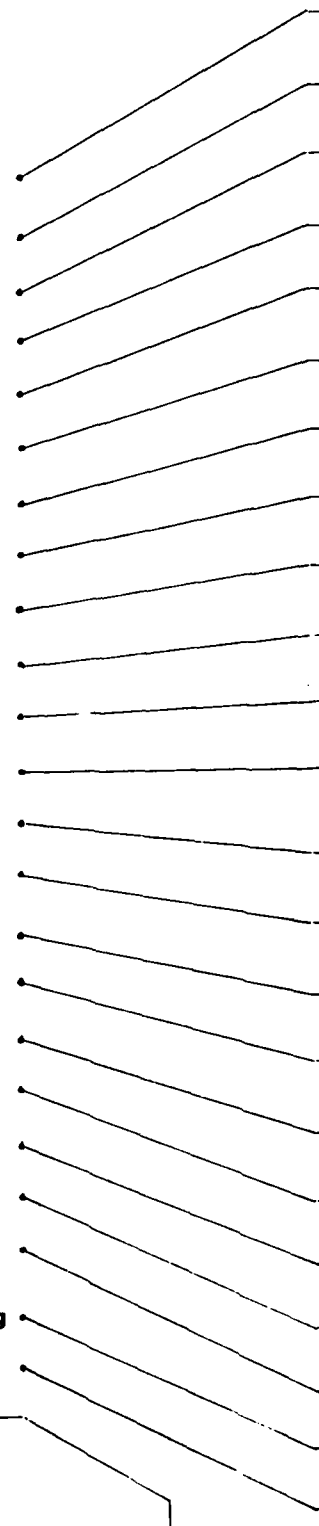
Testing and Characteristics of Coatings

Testing and Characteristics of Electronic  
and Magnetic Materials

Fundamentals of Mechanical Testing and Strengthening

Grain Boundaries

Post Deadline Posters



Electron beam cold hearth melting and refining of superalloys  
for master alloy ingot production.

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The growing demands for saving energy, increasing lifetime and service intervals of critical machinery and engine parts and better housekeeping of strategic metals lead to the demand for alloys of better cleanliness and higher reliability. The application of the Electron Beam Cold Hearth Refining (EBCHR) to produce very clean nickel based superalloys allows the efficient use of recycled foundry scrap or revert alloys. This paper describes the reclamation of superalloys foundry revert by Vacuum Induction Melting plus Electron Beam Cold Hearth Refining used at Degussa AG Hanau and Degussa Electronics Inc., CA, USA. It discusses the economical incentive to use the process. Different process variants were tested in experiments with special reference to the reduction of oxides and the removal of trace elements as well as evaporation losses of alloy components. The results will be discussed and a short outlook on further developments will be given.

CLEANLINESS EVALUATION OF A NICKEL-BASE SUPERALLOY; THE EFFECTS  
OF PROCESS CONTROL DURING ELECTRON BEAM BUTTON MELTING

BY

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Modern process technology has led to substantial improvements in the cleanliness of many advanced alloys. Conventional quality control methods, such as metallography and NDT techniques, are inadequate to assess the very low inclusion contents of these materials ( $< 10$  ppm and  $< 25 \mu\text{m}$  diameter). The Electron Beam Button Melting (EBBM) test is being developed to evaluate the cleanliness of "superclean" materials by concentrating the few inclusions from a large volume of alloy in the final molten "cap" where their size, distribution and chemistry can be analysed more fully. This paper considers the effects of varying the principal process parameters during the EBBM test on the nature of the inclusions collected in the final button "cap" and reviews the advantages and disadvantages of various methods of characterising the inclusions.

Results from two versions of the alloy IN718 with similar nitrogen (80 to 90 ppm) but differing oxygen (8 and 20 ppm) contents will be presented. The influence of process parameters such as electron beam power; processing time, pressure and detailed form of the process cycle will be discussed in relation to the "cap" dimensions and inclusion concentration for different masses of melted buttons. Characterisation of the inclusions by a variety of techniques ranging from optical macroscopy to scanning electron microscopy using a range of imaging methods (secondary, back scattered electrons, specimen current, cathodoluminescence, X-ray analysis) has given information on inclusion types, distribution and chemistry.

Only nitride particles were observed in the low-oxygen alloy, and their size and packing density were sensitive to the detailed process cycle. No oxides were observed in over 60 buttons prepared. The high oxygen alloy, however, consistently exhibited large alumina particles ( $\sim 100 \mu\text{m}$ ) in addition to the nitride inclusions. On the basis of these results it is possible to define optimum process cycles for maximum accumulation of inclusions.

\* This work was partly supported by UK industrial companies: AE Turbine Components Ltd; Cameron Iron Works Ltd; Glossop Superalloys Ltd; Howmet (UK) Inc; INCO Alloys Ltd; Ireland Alloy Ltd; Rolls-Royce plc; Special Melted Products Ltd and Willan Metals Ltd.



THE EFFECT OF ALLOYING ELEMENTS Cu, Fe, Mg ON THE UNIDIRECTIONAL  
SOLIDIFICATION OF Zn- 4 %Al ALLOYS

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The microstructure and phase distribution obtained by steady-state unidirectional solidification of Zn - 4% Al Alloy had been investigated. The effect of alloying elements copper, iron and magnesium on the solidification of Zn - 4% Al grown at controlled growth rates ( $R$ ) and temperature gradients ( $G_s$ ). Microprobe microanalyses had been used to determine distribution of zinc, aluminium, copper, iron and magnesium in different phases.

Alloys were prepared by melting the appropriate amounts of high purity metals in an electrically heated furnace. Each alloy were remelted and filled into alumina tubes of 5 cm, in an electrical furnace equipped with vacuum system. Alumina tubes filled with specific alloy were unidirectionally solidified at controlled growth rates ranging from  $0.8 \times 10^{-4}$  cm/sec to  $8 \times 10^{-4}$  cm/sec and the temperature gradients  $38^\circ\text{C/cm}$  to  $90^\circ\text{C/cm}$ . The sample during growth were quenched into ice-water mixture.

Having subjected metallographic investigation of the samples the interlamellar distance of eutectic phase, the dendrite primary arm spacing and distribution of phases were determined.

The eutectic lamellae became thinner and the interlamellar distance decreased as the growth rate increased. The relation between interlamellar distance and growth rate can be expressed with the following equations:

$$\lambda = \text{constant} \times R^n$$

here  $n$  which depends on temperature gradient increased from 0.34 to 0.41 as  $G_s$  increased from  $38^\circ\text{C/cm}$  to  $90^\circ\text{C/cm}$ .

The interlamellar distance was not influenced by copper upto 1.56 % addition and iron upto 0.10 %. By addition of only 0.06 % Mg to Zn-4%Al sytem a colony eutectic structure was obtained and eutectic lamellae were found to be broken and sometimes transformed into rods in interdendritic areas.

Primary dendrite arm spacing was related as

$$d \propto (G_s \times R)^{-n}$$

The exponent ( $n$ ) depends on alloy composition

for example	0.1 % Cu	$n = 0.19$
	0.75 % Cu	$n = 0.22$
	1.56 % Cu	$n = 0.28$
	0.10 % Fe	$n = 0.22$
	0.06 % Mg	$n = 0.20$

At growth rates lower than  $2 \times 10^{-4}$  cm/sec dendritic structure transformed to cellular-dendrite

THE GRAIN REFINEMENT OF Al-Cu-Zn ALLOYS  
BY LOW FREQUENCY VIBRATION

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In paralel to development in industry, the attempts to improve mechanical properties are attracted attention of researchers . In considering methods of improving the properties of cast metal, grain refinement by application of low frequency vibration during solidification is of great importance. In the present work the investigation of varying frequencies and amplitudes was carried out on solidifying aluminium copper zinc alloys for varying pouring temperature and mould temperature.

The typical analysis was chosen as Al-4 %Cu- 4% Zn and Al- 5% Cu-10 % Zn. These alloys melted in a electrical resistance furnace and cast into preheated graphite mould. The mould vibrated in the range of frequencies upto 71 Hz with amplitude ranging between 0 and 7 mm . The influence of pouring temperatures between 650°C and 775°C were evaluated with moulds being preheated temperatures ranging between 135°C and 385°C .

The influence of vibration frequency has been found to be more effective than amplitude for Al-Cu-Zn alloys. The application of vibration resulted finer grain structure coupled with a remarkable increase in mechanical properties. The optimum properties of Al- 4% Cu -4 % Zn alloys were obtained with a pouring temperature of 725°C a mould temperature of 285° C, a frequency of 25 Hz and an amplitude of 3 mm. Similar observation for Al- 5% Cu -10 % Zn alloys were made with a pouring temperature of 715°C a mould temperature of 285° C, a frequency of 71 Hz and an amplitude of 2 mm. The application of vibration with higher amplitude increased the problem of porosity, hot tearing and segregation.

**BINDER REMOVAL: THE EFFECT OF BINDER COMPONENTS****K. Lilius, H. Manninen, J. Virolainen**

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Injection moulding of metal and ceramic components is relatively new, but challenging and interesting technology. Metal or ceramic powder is mixed with binder components to form a mouldable feedstock, which is injected into the mould cavities. The binder is then removed from the moulded parts by thermal debinding or solvent extraction. After debinding the parts are sintered to densities near theoretical resulting net-shape or near-net-shape parts.

The choice of binder components has a great effect on the mixing and injection moulding processes, but especially on the binder removal. The binder removal is very critical stage of the process and many defects formed during moulding process, can be noticed only after binder removal. The binder is often a mixture of thermoplastic polymeric materials and some additives.

The behaviour of different types of binder components and their mixtures in binder removal process was investigated in this research work. The effect of binder mixture and parameters of debinding process on the final sintered structure and mechanical properties were also investigated. Two most important factors having effect on binder removal are heating rate and atmosphere. By choosing the right atmosphere the binder removal process can be accelerated. The test materials in this investigation were  $\text{Al}_2\text{O}_3$  and Fe-8%Ni.

Due to the fact that the amount of binder is 20-60 volume percent of the feedstock, the shrinkage of the moulded parts during sintering is large. This might cause warping if the sintering process is not carefully controlled. The sintering process was investigated and optimized in this work by using dilatometric studies and microscopy.

## STUDIES ON THE INTERFACE REACTIONS IN THE REFINING OF METALLIC MELTS BY FILTRATION

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Filtration processes are categorized into two groups: surface filtration and depth filtration. In surface filtration the particles are retained on the surface of the filter. However, in the depth filtration deposition of inclusions occur throughout the depth of the filter. The ability of a filter to remove particles from the melt depends on many factors such as the connection and type of particles in the melt, the melts characteristics (composition, viscosity, surface tension); the temperature and the filter characteristics (composition, structure, permeability).

Two mechanisms predominate in the removal of particles when melts pass through ceramic filter: simple mechanical screening of particle at the surface of the filter and entrapment of smaller particles on the interior surface of the filter. The wettability characteristic of the inclusions with respect to the filter is of paramount importance. If the interfacial energy is high the particles will be pushed out of the melt when they contact another solid surface such as that of the filter material and become attached and bond to the surface.

The objective of the paper is to review some fundamentals of the interface reactions in the refining of metallic melts by filtration. Experimental results of aluminium and steel melts are discussed. The importance of wettability of the filter media to the liquid inclusion and its effect on removal efficiency is presented.

## THE DEVELOPMENT OF WATER SOLUBLE CORES FOR FOUNDRY INDUSTRY

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Production of sodium aluminate -  $\text{CO}_2$  bonded core and mold is investigated. The effects of parameters sodium aluminate mole ratio, its addition percent to sand and gassing time were demonstrated.

A constant water(50 %) and three different mole ratio(1.22, 1.7, 2.0) of sodium aluminate are added to the AFS 53  $\text{SiO}_2$  sand and  $\text{CO}_2$  gas is blown to the 6-8 different multiplies of theoretical minimum values in order to occur its hardening reaction. Pre-gassing is applied during the mixing due to the slow reaction of  $\text{CO}_2$  - sodium aluminate.(Especially for selected mole ratio.) Applied pre-gassing time is 4,8,12,16 seconds for each 1300 gr sand.

As a results of a group of experiments, it is found that sodium aluminate -  $\text{CO}_2$  bonded cores and molds have a medium high temperature/green strength that is similar to the water glass -  $\text{CO}_2$  boded ones.

During manufacturing and casting; these kinds of cores and molds show excellent "water solubility" due to no occur insoluble reaction products. Asencially it obvious that these kinds of cores and molds have also low retain strength.

Using  $\text{SiO}_2$  sand and a systematical gassing and/or pre-gassing treatment are the facts which are used for the first time in our study.

THE PROPERTIES IN THE AS-CAST STATE OF A  
NEW CHROMIUM WHITE IRON

White chromium irons find a large application in the production of abrasion resistant castings, specially as the tools in crushing and grinding equipments. The largest part of chromium iron castings today produced are those with a predominantly martensitic matrix. This implies the necessity of heat treatment of the castings and in connection with this, the necessity of solving of rather complicated relationships regarding chemical composition, hardenability, cooling velocity and cracking susceptibility of the castings.

The present work has investigated the conditions for achieving the predominantly martensitic-carbidic microstructure in a chromium white iron in the as-cast state. The purpose of this investigation was also to establish the abrasion- and impact resistance of a group of chromium white irons on the basis of the abrasion pin-test, dynamic fracture toughness test, dropping ball test and an marked ball test. In the abrasive test the material to be tested is prepared in the form of a cylindrical pin. The loaded pin moves back and forth in a nonoverlapping pattern across a fresh flint abrasive cloth. The dynamic fracture toughness was measured according to ASTM specifications using an instrumented Charpy test machine with a standard size notched specimen. To measure the resistance to repeated impact of materials investigated, a ball dropping machine was used. The test balls are lifted to a height of 6,4 m and allowed to fall freely on a rigid, hard anvil. The impact cycles are repeated until 10.000 drops respectively until the ball breaks. The balls were also tested in an cement mill 4mm in diameter using "marked ball" test.

The obtained results show that by properly alloying it is possible to achieve a predominantly martensitic matrix microstructure in as-cast chromium white iron balls up to 90 mm in diameter. This microstructure show similar or better properties comparing to martensitic-carbidic microstructures obtained with the heat treatment procedures.

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The Alloy Cast Steel Hypereutectoid with Modular Graphite  
of Bainite Martensite Structure in Cast Condition

The technology of alloy cast steel smelting with modular graphite, which got in as-cast condition, of bainite, bainite martensite or martensite structure got in casting, also in cast condition (without heat treatment), has been developed. It has been pointed out, that the modular graphite crystallizes from liquid and austenite in the alloy cast steel; when oxygen content is 18 -:- 55 p.p.m. and sulphur content not more than 0.007 %. The low oxygen and sulphur contents in the alloy cast steel are got through the treatment with synthetic slag in liquid condition. It was found that the decisive effect on the kinetics of the transformation: austenite -> bainite, martensite - is exerted by the microsegregation of elements constituent in the cast steel. The microsegregation is decided by the cooling rate of castings. The microsegregation of carbon, manganese and molybdenum is always straight. The one of silicon, copper and nickel changes in the cooling rate of castings function. When the reverse microsegregation of silicon occurs, the one of copper and nickel is straight, and on the contrary. The transformation: austenite -> bainite, martensite begins in the microregions with increased concentration of silicon and reduced one of copper and nickel. The investigations of the structure constituents and their influence on the mechanical properties of the alloy cast steel have been made. The dependence of the alloy cast steel mechanical properties in the function of its chemical constitution and cooling rate of castings was developed as the algorithm in Basic and Pascal computer languages.

Development of properties and areas of application of graphitic cast irons

Dipl.-Ing. Eberhard Möllmann

Prof. Dr.-Ing. Gerhard Engels

Dr.-Ing. habil. Klaus Herfurth (presenter)

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Discussion of the metallographic fundamentals of the graphitic grey, malleable, SG and vermicular cast irons, which can be interpreted as the "naturally" occurring and objectively influenceable metallic particle compound materials. Consideration of factors of influence that determine formation of microstructure during solidification and cooling as well as during heat treatment. Variation of graphite formation (lamellar, spheroidal and vermicular graphite, temper carbon), each in accordance with size, shape, amount and distribution of the participating phases results in a further range of adjustable properties that, measured by the tensile strength, extend from 150 to 1 500 N/mm<sup>2</sup>. Because, contrary to steel, the metallographic processes of graphitic cast irons not only proceed in accordance with the stable but also the metastable Fe-C diagram, the breadth of variation for microstructure formation, and consequently the influencing of the properties, is considerably greater than in the "steel corner" of the Fe-C diagram.

Representation of quality development by the weighted average tensile strength in accordance with production shares as a measure of product quality. The advance of cast irons into tensile strength ranges up to 1 500 N/mm<sup>2</sup>, with simultaneously good values for plasticity and toughness, has resulted in numerous substitutions of steel for highly stressed machine components (forgings, steel semis). Information is also presented on production examples for castings in high grade graphitic cast irons that improve the mass-performance ratio and reduce the amount of machining.



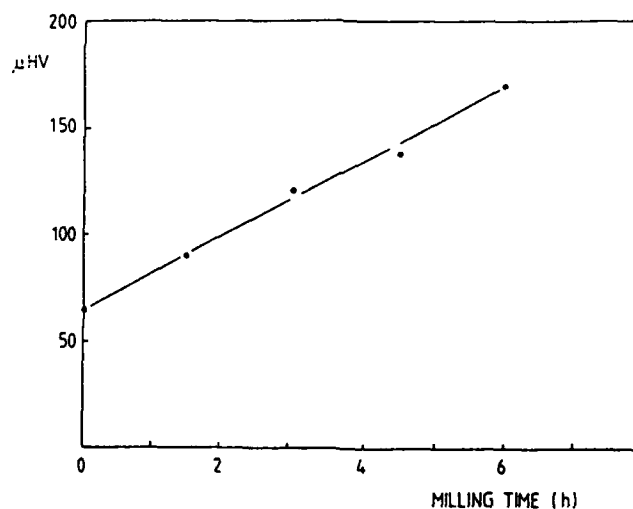
MECHANICAL ALLOYING OF Al-Fe POWDERS

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There is an increasing need for aluminium alloys for intermediate or elevated temperature exposure, their production involves powder metallurgy processing routes. This work is concerned with the development of an Al-Fe alloy for applications between 150 and 350°C. Atomised Al-Fe powders are mechanically alloyed, a process known to enhance the high temperature properties of the alloy. Some of the parameters of the process are discussed related to the microstructural analysis and the measurement of some properties : influence of the milling time, role of the process control agent. The powders are consolidated by hot extrusion or forging. Both microstructural and mechanical properties are presented. This project is supported by the E.E.C. (Euram project on advanced materials).



MECHANICAL ACTIVATION AND MECHANICAL  
ALLOYING OF METALLIC SYSTEMS

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Mechanical activation and mechanical alloying of several metallic systems was investigated. The process was carried out in a vibro mill under different experimental conditions. The experimental results of the process and the characterization of the products by means of X-ray, DTA and electron microscopy are reported.

### II.3

#### Characteristics of very fine metal powders produced by a two-step atomization technique

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The success of PM processing often depends on the production of fine, high quality atomized powders in both low and high production quantities. The development of two-step gas/water atomization techniques offers the opportunity for improved powder characteristics compared to those produced by simple gas atomization or water atomization techniques. Gas atomization can be used to produce very fine powders, but powder cooling rates are limited because of the relatively low convection heat transfer coefficients. Although heat can be extracted more rapidly during water atomization, it is nevertheless difficult to produce fine powders. Powder oxygen levels can also be quite high for water atomized powders. In this study, two-step gas/water atomization technique have been developed to produce very fine, rapidly quenched powders. Oxygen levels of produced powders were low minimizing costs associated with the subsequent reducing step. Results were compared to powders produced by simple gas atomization and simple water atomization. It is expected that two-step atomization can also be used to produce powders from alloys that are difficult to successfully water atomize.

The two-step gas/water atomization process begins with disintegration and initial atomization of a liquid metal stream by high velocity gas-jets. A concentric high velocity waterjet pattern impinges on the gas atomized particles a short distance beyond the initial atomization region rapidly quenching the liquid particles. Important limitations of simple gas or water atomization techniques can be to a certain extent overcome. The collision of liquid particles during simple gas atomization is significant and increases the average particle size considerably prior to particle solidification. Stream break up during water atomization is inefficient also resulting in large particle sizes. However during two stage atomization, the fine initial gas atomized liquid is quickly water quenched resulting in an overall decrease in the average particle size and an agglomeration of solidified and partially solidified fine particle rather than the formation of large spherical powders. Results for the two stage atomization of a Cu-6 % Sn alloy are reported. Mean particle diameter of less than 25  $\mu\text{m}$  have been achieved with cooling rates of  $10^3 - 10^6 \text{ K/s}$  resulting in typical secondary dendrite arm spacings of 0.7  $\mu\text{m}$ . Powder oxygen levels for gas/water atomized Cu-6 % Sn were 90 % less than for water atomization alone. The unique particle morphologies observed during two-stage atomization also resulted in increases in the green strength of the consolidated powder.

Theoretical models have been developed to predict liquid stream disintegration and particle solidification rates for two-stage atomization. Good agreement has been achieved between cooling rate predictions from the model and cooling rates measured experimentally from secondary dendrite arm spacings.

NEW GAS ATOMISATION NOZZLES  
FOR ULTRAFINE METAL POWDERS PRODUCTION

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During past years, ONERA Materials Department has set up all the devices required for the study of prealloyed powders metallurgy. Among these, a gas atomisation tower has been built to produce nickel base alloy powders. The fineness of the powder is drastically connected to the nozzle performances.

The metallurgy know-how linked to the aerodynamic knowledge of ONERA lead to the design of a new nozzle generation. With these new nozzles, the mean diameter of the nickel base alloy powders is as low as 27  $\mu\text{m}$ .

These performances are obtained with:

- a new nozzle thinner throat which lowers the gas consumption and allows higher metal flow rates;
- gas flow visualisation tests by laser tomography.

Moreover, through a suitable ceramic selection for the crucible and the increase in the vacuum "cleanness" before atomisation, the powder contaminations by, respectively, ceramic inclusions and oxygen, were severely reduced. For example, the oxygen content of powders from 32 to 40  $\mu\text{m}$  is lower than 75 ppm.

The demand for always finer powders is necessary to increase the high temperature turbine disks performances.

Their initiation fatigue resistance being limited by the maximum diameter of ceramic inclusion, the powders have to be sieved. In order to increase the yield, the powders must be finer.

The interest for fine powders is not only needed for high temperature turbine disks, but also for injection moulding, brazing and plasma spraying, which represent attractive applications for these gas atomisation nozzles. Their development will carry on for industrial applications in ONERA.

THE MORPHOLOGY AND THE STRUCTURE OF POWDERS OBTAINED BY  
WATER ATOMIZATION OF SOME NICKEL ALLOYS

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We studied the conditions necessary to obtain hollow powders by water atomization. The paper also presents the structure of the surface and the interior of the powders obtained, the grain size and the bulk density. The powders have the grain size within the range of 0.045 to 1.5 mm. We used in our testing the water atomization at 60 to 120 bar, of a nickel-silicon-boron-chromium alloy, overheated at 1640 to 1680 °C.

**Electrophoresis - An Alternative Forming Technique for Sub-micron Ceramic Powders**

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Electrophoresis has been studied in order to prove the possibility of producing compact ceramic bodies with a homogeneous and defect free microstructure from a well defined submicron alumina suspension. Therefore an ethanolic suspension of commercial alumina was developed, which was stabilized by polyacrylic acid. A non aqueous suspension was used to avoid the formation of gas bubbles by the electrolysis of water during the consolidation process. An optimization process resulted in a stable suspension with high solid content and zeta-potential as well as low viscosity. This suspension has been used to examine the principal parameters, which determine the electrophoretic consolidation process. Compact green bodies, 50 mm in diameter and upto 4 mm thick could be produced. The microstructure is homogeneous except a thin porous layer at the electrode facing side. The formation of the porous layer was investigated by different methods and the results of these experiments will be discussed.

**Preparation of Ultrafine Nd-Fe-B Magnetic Particles  
by Chemical Reduction in Microemulsions.**

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**Abstract.**

New powder technology alloys ultrafine Nd-Fe-B magnetic particles to be prepared by chemical reduction at low temperatures ( $275 < T(K) < 375$ ) in water-in-oil microemulsions<sup>1</sup>. The reaction takes place inside water droplets where size (a function of the composition and temperature of the microemulsion) controls that of the particles produced. Aggregation can take place by both diffusion-limited and reaction-limited processes, and a variety of aggregate types ranging from fractal to compact structures<sup>2</sup> has been produced. Some of the magnetic properties of the particles are reported.

<sup>1</sup> M.A. López-Quintela, J. Rivas and J. Quibén, spanish patent proposal nr. 8803592.

<sup>2</sup> P. Meakin, Phys. Rev. A, 27, 604, 1495 (1983).

## PREPARATION OF MIXED Mg-Fe HYDROXIDES FOR Mg-Fe SPINEL FORMATION

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The  $\text{MgFe}_2\text{O}_4$  spinel applications as chemical humidity sensor stimulated this research, whose aim was to get the synthesis of the spinel from coprecipitated Mg-Fe hydroxides. Different parameters were studied in order to define the conditions leading to the most suitable microstructural characteristics of the spinel. The mixtures of  $\text{Mg}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  were obtained by coprecipitation from aqueous solution of the corresponding salts (nitrates, chlorides). The influence of precipitation parameters (temperature, molar concentration and the molar ratio of the salts) were investigated.

Thermal decomposition of the single and mixed hydroxides and the synthesis of the spinel were characterized by thermal analysis, X-ray diffraction and SEM.

The  $\text{MgFe}_2\text{O}_4$  was obtained also by thermal decomposition of mechanical mixtures of  $\text{Fe}(\text{OH})_3$ - $\text{Mg}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ - $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$ - $\text{Mg}(\text{OH})_2$  and  $\text{Fe}_2\text{O}_3$ - $\text{MgO}$  with the molar ratio  $n\text{Fe}/n\text{Mg}$  2:1.



Electrochemical alloying of nickel and copper to prepare Fe-Ni-Cu powdermetallurgical systems.

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The most simple and at the same time the frequently employed technique to prepare powder metallurgical systems is mechanical mixing of the basic metall with alloying elements. This method however, besides incontestable advantages has some significant disadvantages. Mechanical mixing namely does not allow to get fully homogeneous distribution of alloying elements in the system. In addition to it in the following technological operations e.g. charging into the pressing tools, mechanical segregation of alloying elements may occur.

Electrochemical alloying presented in this paper, on the other hand, results in homogeneous composition of the powder mixture, having positive influence on the mechanical properties of the sintered products.

The described method to prepare Fe-Ni-Cu powdermetallurgical system is based on cementation and electrowinning processes. The alloying elements nickel and copper create on the iron matrix thin layers, Thus their homogeneous distribution is guaranteed.

Furthermore in the paper the microstructure of the alloyed particles, structure and mechanical properties of the sintered products are discussed.

For preparing the studied system also secondary raw materials, as waste electrolyte from copper refining processes, can be used.

The presented technique is covered by ČSSR patent.

### III.1

#### SURFACE THERMOMECHANICAL TREATMENT (STMT) AS A MEANS TO IMPROVE THE SERVICE BEHAVIOUR OF MATERIALS

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The Surface Thermo-Mechanical Treatment (STMT) can be applied to metal parts to improve their fatigue properties. It is a combination of thermal and mechanical treatment, e.g. inductive surface hardening and rolling. As a result, the surface layer reveals a very fine grain size.

The fatigue life is increased mainly caused by changes of the microstructure. The residual stresses due to STMT are of the same (compressive) type but of smaller amount compared to conventional hardening. The low-cycle fatigue limit is increased by a factor of 10.

MODIFICATION OF INTERFACE PROPERTIES BY ION BEAM TECHNIQUES

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*The interface between substrate and a surface film can be modified by bombardment of the film with ions of sufficient energy to penetrate through the films into the substrate. Usually the interface region is broadened and the adhesion between film and substrate is greatly enhanced. In addition the structure of the interface region may be modified in a controlled manner. Metastable, amorphous or stable alloys or compounds are formed, depending on the film/substrate combination and the type and energy of the bombarding ions.*

*The potential of two techniques, ion beam mixing and ion beam assisted deposition for tailoring interface and film properties are illustrated by the following examples:*

- Modified adhesion of metal films on metals, polymers and ceramics.*
- Ion beam induced broadening of the interface region as measured by Auger depth profiling and nuclear reaction analysis.*
- Modification of film stress as function of energy and intensity of the bombarding ions.*
- Influence of composition and structure of the interface region on the mechanical and chemical degradation to metals.*

THE EFFECT OF HARDNESS DEPTH ON FATIGUE STRENGTH  
IN NOTCHED CARBURIZING STEEL

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In this work, the effect of hardness depth on the fatigue strength has been studied using case hardened steel C1020. As the notch root radius is an important parameter effecting the stress at the tip, a constant notch root radius was chosen. Test pieces have been carburized to different case depths at 1050°C and have been fatigue tested under rotating bending conditions.

The results show that although the fatigue strength is influenced by case depth, it is more severelly affected by the notch sensitivity *factor*.

### III.4

#### THE EFFECT OF HIGH TEMPERATURE (1050 C) CARBURIZING ON FATIGUE STRENGTH

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In this work, the mechanism of fatigue failure, the methods of increasing fatigue strength and also surface hardening treatments have been investigated. The work aims to find out whether the fatigue strength is increased or decreased by the application of the surface hardening in liquid salt bath which is a method widely used in practice. In particular, carburizing treatments at 1050 C in a salt bath have been carried out and the effects have been investigated. The material used for the tests is the steel ASM 1020.

MAGNETIC-IMPULSIVE PROCESSING OF DEPOSITIONS WITH  
CHANGEABLE PROPERTIES AND THICKNESS

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The possibilities for strengthening of thermal coated depositions with the help of subsequent magnetic-impulsive processing are treated in the paper. An attempt is made, on theoretical grounds, to improve the technology of magnetic-impulsive effect of porous depositions from metals changing their thickness and properties (structure, porosity etc.).

As a result, formulas were developed for the determination of the transversity and intensity of the magnetic field and for the determination of the magnetic force as a function of depth of the deposition. Calculations of the distribution of the effect of the magnetic-impulsive field on porous deposition on steel and bronze are specified.

### INFLUENCE OF SILICON ON THE KINETICS OF THE NITRIDING LAYER GROWTH

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The kinetics of the nitriding layer growth is dependent besides other factors on the composition of steel. Silicon can be one of the alloying elements. There are two contradicting opinions on the influence of Si on the kinetics of the nitriding layer growth in the contemporary literature. According to the first opinion, under constant nitriding conditions silicon reduces the thickness of the layer. According to the second opinion, silicon does not practically influence the nitriding process.

The influence of Si was first investigated for hot working tool steels using a model alloy produced by electro-sinter remelting, additionally alloyed by Si to different mass content. The samples of the mentioned composition after heat refining for hardness were nitrided at temperature  $560 \pm 5$  °C during different time periods. The thickness of the created nitrided layer was measured by two different methods. The experimentally obtained results were worked up by means of regression analysis using the least square method. All the results unambiguously proved that Si negatively influences the kinetics of the nitriding layer growth. The influence was expressed quantitatively. Similar results in the same conditions were obtained for other model alloys and for the construction steel.

## A Novel Microstructure in Rapidly Solidified Al Alloys

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Laser beam's surface remelting is known as a powerful technique of rapid solidification for specifically improving the superficial properties of cast metals. For Al base alloys, for example, hardnesses comparable to steel have been obtained leaving unchanged their bulk mechanical properties. It has been shown that wear and corrosion resistance are also improved. In addition, this technique is easy to perform and can be completely automatised.

However, the formation mechanisms of the new microstructures, responsible for these exceptional properties, are poorly known. We have therefore carried out a detailed study of the rapid solidification of eutectic and dendritic Al-Cu and Al-Fe alloys. Single trace melting was performed using a 1500 W CO<sub>2</sub>-laser with beam speed ranging between 0.1 and 10 m/sec. The advantage of rapid surface remelting, compared to other rapid solidification techniques, is the possibility of determining the local growth rate by measuring the orientation of the microstructure with respect to the laser scanning direction.

Transmission electron microscopy observations have been performed in order to characterise the morphology of the microstructure and to measure the intercellular or interlamellar spacing  $\lambda$  as a function of the solidification velocity  $V$ . For  $V$  less than about 0.5 m/sec, the microstructure are continuous, with small grains parallel to the growth direction and a  $\lambda^2 V = \text{const.}$  relationship is followed. For higher velocities, a new type of microstructure, called banded structure, appears in both alloys. This looks like a regular sequence of dark and white bands, approximately 0.5  $\mu\text{m}$  width and perpendicular to the growth direction. The dark bands are formed with a cellular structure, while the white bands are supersaturated solid solutions. At the same time, the material becomes monocrystalline over large regions. For even higher velocities, the dark band width decreases and complete solid solution is gradually reached.

This type of microstructure is quite new, but appears as a normal transition between dendritic or eutectic growth and complete solid solution. It is not predicted by the models of rapid solidification and further work is needed in order to fully understand its formation mechanism.



PROCESSING OF CERAMIC MATERIALS WITH  
HIGH POWER CO<sub>2</sub> LASER

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Engineering ceramics such as zirconia, alumina, silicon carbide and silicon nitride are rapidly gaining importance for use in advanced technology and in manufacturing. The emergence of these ceramics has highlighted the need for developing a method for cutting, drilling and welding.

The main objectives of this research were to conduct a feasibility study into the cutting of thick commercial ceramics and introduce ceramics welding with a continuous wave CO<sub>2</sub> laser.

LASER MACHINING OF CERAMIC MATERIALS  
WITH HIGH POWER CO<sub>2</sub> LASER

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Materials removal rates are reported for silicon nitride, zirconia and alumina machined with a CO<sub>2</sub> laser as a function of power, cutting speed and atmosphere. The laser was used to heat the surface of a workpiece forming a groove by vapourization. Several shaping operations have been investigated including, turning, kneading and milling.

Laser Interactions with Surfaces and Technological Applications

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This paper describes part of a research program using a 6 kW Co<sub>2</sub> laser in applications involving surface melting. One aspect of this program has dealt with the laser melting of high temperature materials, including Tungsten and High Speed Steel, in a pendant drop melt drag process. This particular study was directed to producing fibres from the liquid by contact of the drop with a rotating disc. The rapidly solidified structures were examined by electron microscopy. High speed photography was employed to observe the behaviour of the fluid metal in contact with the wheel. Fibres of different materials with diameters of 30 - 100  $\mu$ m and lengths up to 20 cm were examined.

The second part of this paper deals with laser interaction with a surface. We have correlated the focal number of the lens, laser power and location of the focal point to show the important parameters determining the change from conduction limited melting to key-holing. This part of the research has looked at melting of surfaces and structures resulting from solidification under laser melting conditions, structures in systems involving Boron, and powder injection of Boron Carbide into surfaces. The experiments were performed on steel and commercial Titanium.

#### IV.1

Application of a Finite Element Model to the Microstructure of a Nickel-based Superalloy with high Volume Fraction of  $\gamma'$ -phase.

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At all temperatures the strength of nickel-based single crystal superalloys containing high volume fractions of  $\gamma'$ -phase is determined to a major extent by properties of the  $\gamma/\gamma'$ -interfaces (1).

Properties of  $\gamma/\gamma'$ - interfaces and of the alloy greatly depend on the misfit between matrix and  $\gamma'$ -phase. Therefore in order to follow the course of deformation processes local variations of internal stresses due to the misfit have to be known in the as annealed condition. In a second step the superposition of external stresses must be considered.

A finite element model (FEM) has been applied to the microstructure, the symmetry of the problem allowing for a restriction to a plane problem and 1/4 of a quadratic  $\gamma'$ -particle and its surrounding matrix. The misfit between  $\gamma'$ -phase and matrix is simulated by assigning different coefficients of thermal expansion to the phases. Different elastic coefficients and Poisson's ratios were taken into account.

With no external stresses acting and a cuboidal  $\gamma'$ - morphology we find that:

1. Stresses inside  $\gamma'$ - precipitates are much lower than in matrix channels.
2. There is a very high pressure build up located in matrix channels at the middle of the precipitates.
3. Considering von Mises stresses a local maximum appears near the edge of the precipitate.

Furthermore the resulting stresses are a function of the shape of the  $\gamma'$ - particle.

#### References

- 1) M.Feller-Kniepmeier, T. Link, V. Gaetano and J. Wortmann.  
Z. Metallkde, in press

## IV.2

### TEMPERATURE- AND STRESS FIELD DURING COOLING OF A GAS TURBINE BLADE AFTER FORGING

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Gas turbine blades should have very low distortion and residual stresses, which are determined by the cooling rate after forging and annealing. The temperature- and stress fields in a 800 mm gas turbine blade, made of a nickelbase alloy, were calculated for air cooling and retarded cooling with a rate of  $20^{\circ}\text{C}/\text{min.}$  by the Finite Element Method. The results are in good agreement with experimental data. A method for estimating the limit cooling rate which leads to residual stresses is presented and the influence of these stresses on high cycle fatigue is discussed.

**SELF DIFFUSION AND KINETICS OF ATOMIC ORDERING  
IN THE  $\gamma$  AND  $\gamma'$  PHASES OF NICKEL BASED MODEL SUPERALLOYS**

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Ni-6at%Al, Ni-10at%Al, Ni-1at%Al-3at%Ti solid solutions and Ni<sub>3</sub>Al (stoichiometric and off-stoichiometric) intermetallic compounds, respectively representing model materials for the  $\gamma$  and  $\gamma'$  phases of nickel-based superalloys, have been investigated for determining their ordering and self-diffusion properties.

The solid solutions exhibited changes in local order in the range 660-750 K which resulted in a decrease of residual electrical resistivity. The Ni<sub>3</sub>Al compounds (24.5 to 26.4at%Al) remain L1<sub>2</sub> long range ordered up to the melting point. However a structural change during isochronal anneals was evidenced by the observation of an increase of the residual electrical resistivity in the temperature range 790-970 K. This reversible variation was attributed to changes in the equilibrium degree of long range order of the materials.

The kinetics of order changes during isothermal treatments were studied in the two types of alloys by residual electrical resistivity measurements. Activation enthalpies for self-diffusion were deduced from the temperature dependence of the relaxation times for ordering.

**Determination of Long Range Order in Ni-base ternary alloys  
by X-ray anomalous diffraction using Synchrotron radiation**

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The knowledge of the preferential occupancy i.e. long range order (LRO) parameters, by ternary additions in  $L1_2$  alloys, is crucial to the understanding of the controlling factors in the alloying behaviour. Such information can be predicted but not accurately derived from the ternary phase diagrams.

X-ray diffraction is used currently to measure the LRO parameter in binary alloys. In ternary alloys there are two independent LRO parameters. The determination of their values is formally possible taking advantage of the variation in the atomic scattering factors due to the anomalous correction. However it is in practice very difficult using the wavelengths available with classical targets. The development of synchrotron facilities opens a new field of investigation giving the possibility of adjusting the wavelength in order to optimize the use of the anomalous scattering. Using such a technique, we have performed a determination of the state of LRO in three ternary alloys :  $Ni_{70}Al_{20}Cr_{10}$ ,  $Ni_{75}Al_{15}Ti_{10}$  and  $(Ni_3Fe)_{96.4}Cr_{3.6}$ .

In the  $NiAlCr$  and  $NiFeCr$  alloys, the Cr atoms occupy both of the sites. The Ni-Al and Ni-Fe order tends to be maximum and Cr is distributed in order to complete the stoichiometry of the phase.

In  $NiAlTi$  alloys, it is generally thought that Ti substitutes exclusively for Al, owing to similar atomic size. Our results show that actually Ti substitutes mostly for Al ; however 37% of the Ti atoms substitutes for Ni in the lattice, thus promoting disorder. Hence, the substitution behaviour is not a single-valued function of the size of the addition and other factors are clearly involved. The substitution behaviour is more complex than is generally thought and further accurate determinations of the long range order parameters are clearly needed in order to get a good understanding of the strengthening due to ternary additions in  $\gamma$  alloys.

COMPOSITION DEPENDENCE OF THE PROPERTIES  
OF IRRADIATION INDUCED DEFECTS  
IN  $\gamma$  Ni(Al),  $\gamma$  Ni(Al,Ti) AND  $\gamma$  Ni<sub>3</sub>Al ALLOYS

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The effect of alloy composition on radiation damage has been investigated in Ni-6at%Al, Ni-10at%Al, Ni-1at%Al-3at%Ti solid solutions and in Ni<sub>3</sub>Al intermetallic compounds (24.5 to 26.4at%Al) by residual electrical resistivity measurements. These materials represent model alloys for the  $\gamma$  matrix and for the  $\gamma'$  hardening phase of nickel-based superalloys. The two types of materials were respectively short range ordered and long range ordered.

The alloys and a pure nickel sample used as reference, were simultaneously irradiated in the temperature range 4.6-9.K by 3 MeV electrons.

In the solid solutions, irradiation produced mainly point defects. During isochronal annealing up to 100 K, a resistivity decrease was observed like in a pure metal which can be attributed to the local recombination of point defects. Above 350 K, a large resistivity increase took place, which indicates an increase in the degree of short range order. This was related to the long range migration of vacancy-type defects. The amplitude and the temperature of this stage were dependent upon the nature and the concentration of the solute.

In the intermetallic compounds, irradiation damage probably consisted in both disordering and point defect production. The recovery spectrum was qualitatively similar to that of pure metals. The structure and the temperature of the recovery stages varied progressively with aluminium concentration. However interstitial and vacancy long range migration contributed to reordering and resulted, at 600 K, in a degree of order higher than the initial one.



The effects of low-dose irradiation on the mechanical properties  
of NiAlTi model superalloys.

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Irradiation can affect the mechanical properties of diphase  $\gamma$ - $\gamma'$  alloys by producing modifications both in the matrix and in the precipitates. In a series of NiAlTi alloys (4.5 to 10.5 at% Al, 2.5 to 7.1 at% Ti), the particle-size dependence of the flow-stress was found to display two different regimes which can be related to deformation occurring predominantly by particle shearing or particle by-passing. This was used to separate the effects of irradiation on the  $\gamma$ -matrix and on the  $\gamma'$  precipitates, by careful control of the microstructure resulting from thermal annealing treatments. The change in room-temperature mechanical properties by 400K electron irradiation was determined in a  $\gamma$ - $\gamma'$  Ni-4.5at%Al-6.5at%Ti alloy. In samples containing large particles, in which the flow stress is a linear function of reciprocal particle size, irradiation produced a hardening of the alloy, probably due to the formation of obstacles to dislocation glide in the  $\gamma$ -matrix. For samples corresponding to the particle-shearing regime, the flow stress is independent of particle size and electron irradiation resulted in a softening of the material. This can be attributed to a disordering of the  $\gamma'$  precipitates, and is consistent with direct determinations of the degree of long-range order in the same alloy irradiated in a High Voltage Electron Microscope.

DEVELOPMENT OF A NEW NICKEL BASED SINGLE CRYSTAL  
TURBINE BLADE ALLOY FOR VERY HIGH TEMPERATURES

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The continued improvement in the performance of gas turbine engines requires a simultaneous increase of their operating temperatures. Such an objective may be partly accomplished by improving the temperature capability of the airfoil materials. The use of single crystal superalloys allows to achieve a 60°C temperature advantage over the conventionally cast superalloys. There is a clear need for further improvement in the high temperature capability of such single crystal alloys.

A new nickel based single crystal superalloy, designated MC2, was specifically developed in order to increase the creep strength at temperatures above 1000°C. The composition does not contain any exotic and expensive element such as rhenium, frequently used in the second generation nickel based single crystal superalloys. The specific gravity of the alloy is 8.6. A wide solution heat treatment window of 25°C facilitates the complete solutioning of the coarse as-cast eutectic  $\gamma'$  pools, thus allowing the subsequent precipitation of a large volume fraction of fine  $\gamma'$  precipitates contributing to the high creep strength.

The creep tests undertaken at temperatures above 1000°C on [001] oriented MC2 single crystals show a 40 to 50°C improvement in the temperature capability over commercial single crystal superalloys such as CMSX-2 or PWA 1480. For instance, the rupture life of the MC2 alloy at 1060°C under a stress of 145 MPa is about the same as that of the CMSX-2 alloy at 1010°C. In the temperature range 760-1000°C, the MC2 alloy exhibits a temperature advantage of 10 to 20°C over that of CMSX-2. The tensile properties have been characterized between room temperature and 1050°C. The 0.2% yield stress is more than 1000 MPa between 20 and 650°C, and attains a maximum of 1270 MPa at 760°C, which is significantly better than for the conventional single crystal superalloys. The high cycle fatigue properties of the MC2 alloy, evaluated at 870°C on smooth specimens, are comparable to those of the other single crystal alloys. The strain-controlled low cycle capability of [001] MC2 single crystals was determined at 760°C. This alloy exhibits a three to four-fold life advantage over the CMSX-2 alloy for a total strain range between 1.2 to 1.6%.

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### The growth of modern superalloy single-crystals

The solidification of superalloys (CM 247 LC and CMSX-3) occurs by constitutional undercooling with a dendrite growth structure. The direction of the dendrites, the morphology, is coupled with the crystallography in such a way, that the axes of the dendrites lie in the  $\langle 100 \rangle$ -direction. The precision of this was examined for different orientations.

It was found, that symmetrical orientations, for example  $\langle 100 \rangle$  or  $\langle 111 \rangle$ , generally retain the orientation during growth. The difference between them is in local changes in orientation.

For example,  $\langle 100 \rangle$ -orientations show in Laue patterns a divergence (reflex groups) of about 4-5 degree, in contrast to  $\langle 111 \rangle$ -crystals, where no changes in orientation (sharp reflexes) was observed.

Local changes in orientation can be caused by defects, for example voids or dislocations, which can even form small angle grain boundaries. We think that the defects are required for the reduction of stresses, which arise during the growth competition of the dendrites.

This seems to be the case for  $\langle 100 \rangle$ -crystals in contrast to  $\langle 111 \rangle$ -crystals, where the dendrites grow according to another geometry. Crystals with an intermediate orientation also appear locally as well as globally in the orientation changes during growth. It appears that the crystals have an tendency to develop in a symmetrical orientation ( $\langle 110 \rangle$  or  $\langle 111 \rangle$ ).

Examination by X-Ray (Laue-patterns) shows, that probably the dendrites rotate around a  $\langle 100 \rangle$ -axis. The driving force for this may be again internal stresses, which should occur, as the examinations of symmetrical orientations show, with a minimum for the  $\langle 111 \rangle$ -crystals, as a result of their special growth geometry.

**"Crystalline quality" of directionally solidified single-grains  
of a nickel-based superalloy.**

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An important stage in manufacturing advanced high temperature turbine blades with nickel-based superalloys is in producing single-grain parts. The absence of grain boundaries greatly increases their mechanical properties and combined with the properties of second generation alloys, will allow a further improvement of the thrust of the jet turbines in the following decade. The practical success of this improvement depends on the crystalline quality of the airfoils, in particular when as-cast : the solidification process must not give rise to the formation of parasite grains or grain boundaries. The quality of the cast parts is checked in production by gammagraphy (for internal defects), by chemical etching of the surface (for sub-grains) and by X-ray diffraction (for crystallographic orientation). When using this last technique, the large size of the diffraction spots show that the crystalline quality of the monograins is usually low. This observation might be related to the common appearance of subgrain boundaries in the complex investment castings used.

The aim of the study is to find the origins of the loss of the crystalline quality of a single grain during its growth from a seed or a grain selector. In the work reported here different techniques for studying the material which were as-cast single-grain samples of alloy AM1 are presented. The techniques which have been tested are either volume or surface related.

Volume measurements were made thanks to a particular diffraction technique which uses gamma radiation. Its principle is similar to X rays diffraction, but the energy of the photons is larger (600 keV). It allows bulk and non destructive studies without surface preparation. Due to the small value of the wavelength (0.02 Å) and consequently to the small value of the BRAGG angle ( $< 1^\circ$ ), this technique is only sensitive to lattice tilt. Furthermore extinction phenomena are often negligible and the diffracted intensity is directly proportional to the diffracting volume. In this case the diffraction pattern corresponds to the mosaïcicity, which is the distribution of the orientations of the lattice planes. Imaging of the volume distribution of the orientation of the planes can be achieved by use of neutron topography : for a given angle the diffracting planes appear as thin volumes elongated parallel to the growth direction. The effect of the solidification conditions, the temperature gradient and the growth velocity, have been studied.

Two surface techniques have been used, namely classical optical micrography and X-ray topography. The first one allows for observations of the dendritic array, with primary trunks appearing after chemical etching. X-ray topography, known as the BERG-BARRETT technique, allows for the study of the angular distribution of the cristallographic planes on the surface. This can be achieved by use of a classical X-ray generator or more conveniently with a Synchrotron. The rocking curves that can be recorded by this technique show a mosaïcicity of the same order of magnitude as measured in volume. The technique allows for imaging the diffracting zones for different angles on the rocking curve : an important result is that these zones are the dendrite trunks that are observed on the optical micrographs. Thus this technique appears a convenient way for establishing the relation between the solidification process of dendritic structures and their crystalline quality.

Usefulness of these different techniques and comparison of their possibilities will be discussed. An attempt was made to find a relation between surface and volume observations, in particular at the scale of the dendrites.

# **HIGH TEMPERATURE STRESS-INDUCED SPREADING OF SISF IN THE $\gamma'$ PHASE OF THE CMSX2 SUPERALLOY**

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## **Introduction**

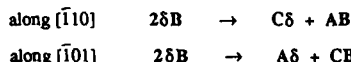
After static experiments at room temperature, the presence of SISF, in L12 ordered alloys, has been reported to be produced by deformation. However, the necessary conditions of stress and temperature for their nucleation to occur is up to now rather unclear. Though leading to very low strain rates, the propagation of these faults appears to be of major importance in the plasticity of these engineering materials. Described in this article are the determination of the intrinsic nature of the stacking faults produced by "in situ" straining of the  $\gamma$  phase (type Ni<sub>3</sub>Al) together with the stress-induced spreading of the faults at high temperature.

## **Observations**

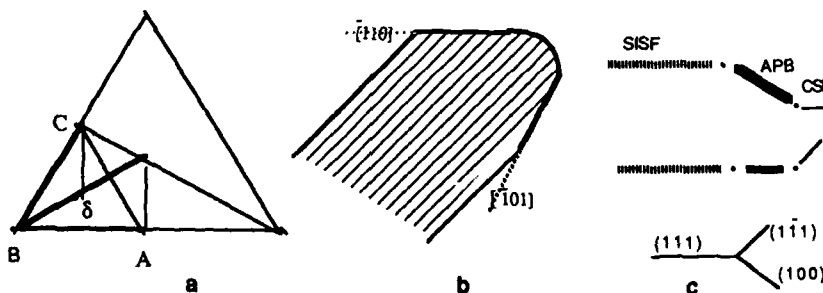
- The nature of the stacking faults is TEM investigated on the basis of the dynamical theory of the electron diffraction by a fringe contrast analysis.
- Dynamic "in situ" sequences at four distinct temperatures (675, 735, 870 et 920°C) are reported:
  - the spreading of the stacking faults ( $2AB \rightarrow 2A\delta + SISF + 2\delta B$ ) (a) occurs with the moving super-Shockley mostly lying in two  $\langle 110 \rangle$  type directions (b) (namely  $\bar{1}\bar{1}0$  and  $\bar{1}0\bar{1}$ ).
  - for a constant applied stress, the velocity of the super-Shockley is constant at a given temperature.
  - the velocity of the super-Shockley exhibits a linear dependence on temperature (from 5 Å/s at 675°C to 120 Å/s at 920°C). This leads to the activation energy of the slip mechanism.

## **Discussion**

- Stacking faults in deformed  $\gamma'$  phase are mostly of intrinsic nature.
- The straightness of the super-Shockley lying along the  $\langle 110 \rangle$  directions may be explained by the following core dissociations (a):



Shown in (c) is the geometry of the possible core configurations. Unfortunately, the working resolution is too low to conclude which one do really occur.



However, to explain both the alignment along the  $\langle 110 \rangle$  type directions and the viscous thermally activated motion of the super-Shockley, we propose a locking/unlocking mechanism in which locking would occur at each atomic row and unlocking would be thermally activated. The activation energy of such a mechanism is estimated to 1.38 eV. In addition, the nucleation of a SISF from the local pinning of a superdislocation has been investigated. This corresponds to the initial step of the creation of a mechanical twin in this alloy.

## CREEP ANISOTROPY OF SINGLE-CRYSTALLINE SUPERALLOYS

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Modern single-crystalline turbine blade materials exhibit outstanding high-temperature capability which has been achieved by a consequent readjustment of alloy composition and processing. High creep strength at intermediate temperatures, in terms of stress rupture time, however is limited to  $\langle 001 \rangle$  directions. Stress rupture lives in  $\langle 011 \rangle$  and  $\langle 111 \rangle$  orientations can be more than 10 times less than along  $\langle 001 \rangle$  and have become of serious concern in blade design where multiaxial stress states owing to airfoil bending, thermal gradients and blade geometry have to be dealt with. This paper focusses on the change in creep anisotropy, especially the surprising weakness in  $\langle 111 \rangle$  direction appearing in recent single-crystalline superalloys as a result of compositional and processing modifications. The paper elucidates the effect of  $\gamma'/\text{Ni}_3\text{Al}$  shape and distribution and in this way complements a recent paper by Caron et al. associating creep anisotropy with  $\gamma'$  size and spacing<sup>1)</sup>.

Our investigations concerning the creep behaviour at 750 °C of CM 247 LC and CMSX 3 single crystals in  $\langle 001 \rangle$  and  $\langle 111 \rangle$  orientations indicate that the onset and the efficiency of work-hardening in primary creep are most decisive for stress rupture life, independent of the heat treatment through which the alloy has gone. Steady-state creep rates for  $\langle 100 \rangle$  oriented crystals with different  $\gamma'$  distributions are identical. The corresponding creep tests for  $\langle 111 \rangle$  orientation are underway. In CM 247 LC alloy with a  $\gamma'$  particle size of about 0.5  $\mu\text{m}$ , stress rupture life in  $\langle 111 \rangle$  orientation is still superior compared to  $\langle 100 \rangle$  oriented crystals. Alloys with particle sizes of 0.5  $\mu\text{m}$  therefore cannot be considered as generally yielding poor stress rupture lives in  $\langle 111 \rangle$  orientation as might be inferred from reference <sup>1)</sup>. Metallographic examination concerning the localisation of plastic deformation in  $\langle 100 \rangle$  and  $\langle 111 \rangle$  oriented crystals has shown that, in addition to particle size and spacing, the  $\gamma'$  morphology is an essential parameter in determining creep anisotropy. A critical assessment concerning the influence of  $\gamma'$  shape, size and spatial distribution on creep anisotropy and related dislocation mechanisms will be presented.

- 1) P. Caron, Y. Ohta, Y.G. Nakagawa and T. Khan; in "Superalloys 1988", ed. by S. Reichman et al., The Metallurgical Society, 1988.

## CHEMICAL SEGREGATION AND PRECIPITATION PROCESS IN SINGLE CRYSTAL NICKEL-BASED SUPERALLOYS

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The casting process used for manufacturing single crystal turbine blades with nickel-based superalloys involves a dendritic solidification front which finally leads to chemical microsegregations. These heterogeneities at the scale of the dendrites are not completely smoothed out by the further standard heat treatments. However the material is generally considered afterwards as being homogeneous with regard to its service behaviour.

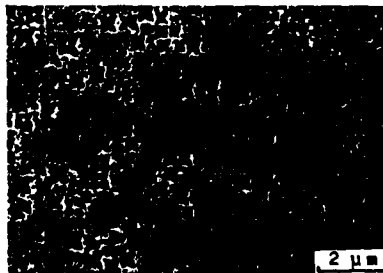
The present work focused on the influence of the residual chemical segregations on the  $\gamma'$  precipitation kinetics, the final microstructures and the further behaviour of the material.

Two commercial superalloys have been used, both presenting three levels of chemical homogeneity : i) as cast ; ii) after a standard homogenization treatment, i.e. 3 hours above the  $\gamma'$  solvus ; iii) after a 100 hours homogenization treatment. By automatic microprobe analysis, the material was shown to be homogeneous after the third treatment while some elements still presented a noticeable variability after the second one.

The  $\gamma \rightarrow \gamma + \gamma'$  transformation was studied by performing two types of precipitation treatments: i) continuous cooling from the  $\gamma$  domain ; ii) isothermal treatment just below the  $\gamma'$  solvus. The transformation was followed by D.T.A. and dilatometry. It was also possible to quench the metal at different times of the treatments in order to visualize the microstructural evolution by electron microscopy. The very well homogenized alloy was used to measure the precipitation kinetics and to characterize the growth mechanisms which involve successive shape changes. In the case of non homogeneous alloys, the experiments pointed out that even a very slight chemical segregation leads to important differences in the precipitation kinetics, which can result in a scattering of the final precipitate morphology.

The possible consequences of this non homogeneous microstructure will be discussed in the light of two types of experiments: i) isothermal aging without any applied stress ; ii) compression and compression-creep tests on both homogeneous and non homogeneous alloys (experiments still in progress).

Microstructure of a sample quenched in the precipitation range. The alloy had been previously homogenized for 3 hours at 1300°C. The differences in volume fraction and morphology of the precipitates result from a local chemical gradient (horizontal on this micrograph).



# COARSENING KINETICS AND MORPHOLOGICAL CHANGES OF THE $\gamma$ PHASE IN A SINGLE CRYSTAL NICKEL-BASED SUPERALLOY

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The  $\gamma$  -  $\gamma'$  microstructure of single crystal nickel-based superalloys can undergo drastic changes during high temperature heat treatments, even in the lack of any applied stress. A quantitative characterization of the phenomena involved is interesting for both a theoretical and a practical point of view ( study of the Oswald ripening mechanism, prediction of the service behaviour ).

The present work dealt with the structural evolution of a commercial superalloy, AM1, during an isothermal high temperature heat treatment. Single crystal samples, with different initial microstructures resulting from various thermal histories, were kept at 1100°C for different times up to 1500 hours. The resulting microstructures were then observed by scanning electron microscopy.

The aging treatment resulted in both coarsening and "raftening" of the  $\gamma$  phase. The coarsening kinetics were characterized by automatic image analysis. The size distribution was measured at the different aging times using an image processing algorithm based on successive "binary openings with a square structuring element". During the first times of the aging treatment the coarsening kinetics were found to be consistent with the classical theories relative to Oswald ripening. However after a few hundred hours the measured mean size increased less rapidly as expected. This slowing down of the coarsening seems to be related to the outset of changes in the shape of the precipitates from a cuboidal to a plate like morphology. The change of equilibrium shape with increasing size is predict by several theoretical works in the case of alloys with low amount of precipitates. Some authors also linked these morphological changes with a progressive loss of coherency at the  $\gamma$  -  $\gamma'$  interface. At this time we are working in this direction.

In the lack of any applied stress, the raftening which appeared for the longer aging times was thought to develop evenly in the three possible {100} planes of the crystal lattice. However it was observed that preferential orientations of the  $\gamma'$  rafts could be selected locally under the action of even a very slight chemical gradient, such as the one resulting from the single crystal casting process. This leads to  $\gamma'$  rafts periodically oriented at the scale of the solidification dendrites. An attempt will be made to explain this phenomenon in the light of recent works concerning the morphological developments during diffusion growth.



## Elastic Properties and Microstructure of Nickel-Base Superalloys at High Temperature

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The calculation of resonance frequencies and stress-strain behaviour of turbine blades is based on the knowledge of the elastic properties Young's modulus  $E$ , shear modulus  $G$ , Poisson's ratio  $\nu$  and the orientation dependent compliances  $S'_{ij}$  ( $1/S'_{11} = E$ ;  $1/S'_{44} = G$ ;  $-S'_{12}/S'_{11} = \nu$ ) of the employed superalloys. Engineering superalloys are often available as monocrystalline, directionally solidified, texturized and texture-free polycrystalline modifications of the same material. For the design of statically and dynamically loaded turbine structures the dependencies of elastic properties of applied superalloys on temperature and microstructure such as orientation of single crystals, grain arrangements and contributions of metallurgical phases are of great interest.

The Förster resonance method allows reproducible measurements of  $E$  and  $G$  up to 1200°C. The orientation dependencies of the Young's and shear modulus of the monocrystalline superalloys MAR-M002 mod. and CMSX-6 are determined experimentally. Taking the coupling of vibrations into account the orientation-independent compliances  $S_{ij}$  in  $\langle 100 \rangle$  are calculated by means of linear regression.

The experimentally observed variations of the elastic properties of polycrystalline alloys (MAR-M247, IN 738) can be explained reasonably by the application of several known structure-correlated boundary concepts using the mentioned coefficients  $S_{ij}$  of the single crystals.

An additional goal of this paper is to point out that the temperature behaviour of elastic properties of superalloys can be calculated approximately by suitable rules of mixture. Theoretical calculations are applied, using the experimentally determined modulus of special model-alloys, namely:  $\text{Ni}_3\text{Al}$ ,  $\text{Ni-Cr-Co-W}$  and  $\text{TiC}$ , representing  $\gamma'$ -precipitates,  $\gamma$ -matrix material and carbides, respectively.

## Measured and Calculated Elastic Properties of Directionally Solidified Ni-Base Superalloys

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The orientation dependence of the elastic properties of IN 738 LC DS was investigated by the resonance method in the temperature range from 25° to 1150°C. To give a quantitative description of these results, different models for the calculation of the elastic moduli for different orientations with respect to the growth direction were applied. Under idealised conditions they can be calculated by averaging the elastic moduli of a number of cubic single crystals. For the  $\langle 001 \rangle$  growth direction the orientation of the single crystals must be chosen corresponding to the ideal  $\langle 001 \rangle$ -fibre texture. Different averaging methods are possible. For non-ideal  $\langle 001 \rangle$ -fibre textures the difference to the ideal elastic behaviour can be described by the model of hexagonal symmetry, if the orientation-distribution-function (ODF) is known. For IN 738 LC DS it could be shown that the calculated curves agree well with the measurements. For this material the calculations for the ideal  $\langle 001 \rangle$ -fibre texture and for the measured texture, described by the ODF, show small differences.

From measurements of the elastic properties of directionally solidified alloys with ideal  $\langle 001 \rangle$ -fibre texture the three elastic constants  $S_{11}$ ,  $S_{12}$  and  $S_{44}$  of the corresponding cubic single crystal can be determined. This method was derived and applied to IN 738 LC. The mentioned elastic constants obtained from this calculation and from single crystal measurements show good agreement. This is of great importance for the calculation of the elastic properties of polycrystalline alloys which are not available as single crystals.

TEMPERATURE DEPENDENCE OF STRESS RESPONSE AND MICROSTRUCTURAL  
EVOLUTION IN NIMONIC PE 16 UNDER LOW CYCLE FATIGUE LOADING

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Low Cycle Fatigue (LCF) behaviour of a nickel base alloy, Nimonic PE 16, strengthened by the precipitation of  $\gamma'$  phase having  $L1_2$  structure and  $Ni_3$  (Al, Ti) composition, has been investigated as a function of the following parameters: The size of  $\gamma'$  precipitates (10 - 57 nm), the nominal total strain range (0.88% to 5.0%) and the temperature (25° to 650°C). For all test conditions, the material shows an initial cyclic hardening. This is followed by softening for small  $\gamma'$  particle sizes and a stable stress response for large  $\gamma'$  particle sizes. The particle size at which the transition to stable behaviour occurs is larger at lower testing temperatures. The microstructural evolution also reveals a similar temperature dependent behaviour. The stable stress response is characterised by a uniform distribution of dislocations in the matrix with loops around  $\gamma'$  particles. In the case of unstable stress response, deformation is confined to bands, their width being extremely thin at 650°C and increasing with decrease of temperature.  $\gamma'$  particles are sheared by the thin bands at 650°C whereas at room temperature, these bands are devoid of  $\gamma'$  precipitates. At intermediate temperatures extremely fine  $\gamma'$  particles are observed within these bands. These results are interpreted in terms of different mechanisms of dislocation-precipitate interaction and fatigue induced precipitation.

Examination of Creep-Fatigue Crack Growth  
in Alloy 800 at 700°C

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To investigate the crack growth behaviour under combined creep-fatigue loading, CT 25mm-specimens of X10NiCrAlTi 32 20 (Alloy 800) have been tested in experiments with cyclic loadings and hold times, with static loadings and short stress relief interrupts, with ramp type loadings, and with sequences of separate fatigue and creep crack growth periods. The test temperature of 700°C was selected because only in this temperature range this alloy provides similar amounts of crack growth under creep and fatigue conditions due to equivalent stress levels. For the estimation of crack growth under combined loading conditions a linear accumulation of increase in crack length was proved using the crack growth laws of pure creep and fatigue crack growth.

Microstructural examination of the crack front clearly differs between fatigue type transgranular and creep type intergranular crack growth.

Hold time and ramp loadings lead to a higher crack growth rate compared with pure creep or pure fatigue crack growth tests. In hold time experiments the crack growth rate is higher than in ramp tests with the same period time. The results of hold time tests can be fairly enough predicted by linear damage accumulation rules.

Authors: Dr.-Ing. Karl Schreck  
Dipl.-Ing. Martin Spaniol

Improvement of the static and dynamic strength characteristics  
of Nickel Base Cast Alloys

Conventionally cast, integral turbine wheels have a very inhomogeneous macrostructure in the hub area. Also the formation of pores is unavoidable in this area. Both pores and the inhomogeneous structure negatively affect the static and dynamic strength characteristics.

Improvement of those characteristics can be realized by use of a special pouring technique in connection with the hot isostatic pressure (HIP) technique.

The improved homogeneity of the structure is the result of a specially developed pouring technique. The extended occurrence of microporosity accompanied by that can be compensated by a hot isostatic pressure step following the pouring procedure. The hot isostatic pressure step here shall be considered as a heat treatment. In the following the complete procedure is called FK HIP.

The FK HIP procedure has been used with two different materials but components of similar geometry: INCO 713 LC (WL 2.4670) and MAR 247 LC. Basically the procedure was left unchanged in both cases, only the parameters need to be adjusted dependent on the material.

For evaluation of the results comparison values were available from conventional pouring technique. All values have been obtained from samples taken out of the component. In case of the material INCO 713 LC the FK-HIP procedure can be directly compared with the conventional pouring technique.

The material MAR M 247 LC has been conventionally poured in its version with the higher carbon content (MAR M 247), which means, that apart from the changed manufacturing procedure also the material modification may play its part.

Significantly improved static and dynamic strength characteristics resulted for the material INCO 713 LC by use of the FK-HIP procedure. Due to the very homogeneous macrostructure the scattering of the characteristics has been reduced drastically. Without any exception the improvements can be attributed to the FK-HIP procedure.

The same behaviour of the characteristics has been observed with the material MAR M 247 LC after having passed the FK-HIP procedure, but the improvement of the characteristics can not be exclusively attributed to the FK-HIP procedure.

DESIGN, DEVELOPMENT, STRUCTURE AND PROPERTIES OF  
NEW ADVANCED NICKEL BASE ALLOYS AND OTHER MATERIALS

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During the past thirty-five years the author has mainly been concerned with the design, development, structure and properties of advanced nickel base alloys. More recently, a new range of advanced stainless steels, high speed steels and sintered carbides has been developed. A new series of binary, ternary and more complex nickel base alloys has been produced using powder metallurgy and concepts of solid solution strengthening, dispersion strengthening and precipitation hardening. High purity powders of nickel, nickel/chromium, stainless steel, high-speed steels and stable carbides such as TaC, TiC, NbC, stable borides  $\text{TiB}_2$ , nitrides, oxides and silicides have been used. The alloys were prepared using standard powder metallurgy methods of cold isostatic pressing, low and high temperature sintering, either in vacuum or controlled atmospheres; some alloys were subjected to hot isostatic pressing at 1300 °C to give theoretical density and improved metallographic structures. A major part of this work has been to develop built-in oxidation resistance in the alloys for high temperature use (1150 °C in air for > 100 h).

Microstructural Characteristics of an Ethylene Cracking Pipe

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Centrifugally cast Fe-Ni-Cr superalloys are generally chosen for the cracking pipes in the pyrolysis units for the production of ethylene from naphtha. Internal carburization is one of the main problems encountered in such pipes in the petrochemical industry. The present work was undertaken to shed some light on this matter.

The Fe-Ni-Cr superalloy used had the following chemical composition: 0.41%C, 27%Cr, 32%Ni, 1.5%Nb, 1%Mn, 1.9%Si. The centrifugally cast pipe samples were in two different conditions: one as-cast and the other had been taken out of service after 2 years and 17 decoking operations. Suitable specimens were prepared and the microstructures were studied metallographically.

The as-cast pipe had the usual dendritic cell structure with eutectic carbide networks and exhibited the same microstructure throughout its thickness. SEM studies showed the existence of two different types of carbides which were largely precipitated on grain and dendritic cell boundaries. Elemental x-ray mapping indicated that the coarse skeletal carbides (5-40  $\mu\text{m}$ ) contained Cr; those finer ones (<2  $\mu\text{m}$ ) contained Nb. X-ray diffraction studies of electrolytically extracted carbides proved the existence of only the  $\text{M}_7\text{C}_3$  and MC type carbides. In the used pipe the dendritic cell structure had mainly remained but the subsurface had a carbide-free zone of about 200  $\mu\text{m}$  width. The inner surface had a 15-30  $\mu\text{m}$  thick oxide layer which consisted mostly of  $\text{Cr}_2\text{O}_3$  with occasional Fe possibly indicating the existence of a spinel. Directly underneath this surface oxide layer lay branchy intrusions of  $\text{SiO}_2$ . The carbide-free zone contained no Cr-carbides but exhibited a decreased quantity of MC precipitates. Within the central regions of the thickness of the pipe the dendritic cell structure still appeared but the carbides had increased both in volume and size; intracellular precipitation had also taken place. SEM studies clearly showed that the morphology of the eutectic carbides had changed very much: There were large globular carbides as well as small individual precipitates. Point analysis of the globular precipitates mainly contained Cr whilst the small ones Nb. X-ray diffraction studies of the electrolytically extracted carbides proved the existence of the  $\text{M}_{23}\text{C}_6$  and the MC type carbides only. The wt % of the extracted carbides had increased from 4.9% in the as-cast microstructure to 9.6% in the as-used one indicating that more carbide precipitation occurred at 1100°C.

# Metal Ceramic Composites for High Temperature Applications

(P. von den Brincken, P. Busse, P. R. Sahm)

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## Basic Idea:

Plastic deformation and destruction of metallic high temperature components (e.g. gas turbine blades) starts at the weakest points of the microstructure:

- the grain boundaries ( → grain boundary sliding)
- the inevitable lattice defects ( → dislocation sliding).

Grain boundaries as two-dimensional „bottle necks“ are avoidable. The production of single crystalline components by means of „directional solidification“ (figure 1) as well as the production of polycrystalline ODS-material (figure 2) is already possible.

## Conclusion:

The single crystalline matrix of such a material (e.g. a superalloy) should be reinforced by a homogeneous distribution of very fine grained ( $< 1 \mu\text{m}$ ) ceramic particles (figure 3). They must have a minimum distance without contacting each other (figure 4).

## Necessary boundary conditions:

1. At this time solidification of a dispersion reinforced matrix is only possible under microgravity conditions (see table 1). In the earth laboratory, metal and ceramic may segregate due to buoyancy. Additionally, gravity-induced thermal micro-convections lead to collisions and agglomerations of the particles.
2. To obtain an engulfment of the particles during crystallisation, the velocity of the solidification front has to exceed a critical value  $v_c$  (figure 5). This critical growth rate is a function of the interfacial energies  $\gamma_{ij}$ , the viscosity of the melt  $\eta$ , and the particle diameter  $d_p$  (figure 6).
3. The ceramic powder has to be wetted by the liquid metal (figure 7-12). Otherwise the particles would agglomerate and the strengthening effect would be lost. The study of the wetting behavior, e.g. between oxide ceramic and nickel-base-superalloy, is one of the main research topics at ACCESS.

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MAN-Technology (Munich)  
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## CREEP BEHAVIOUR OF A HEAT RESISTANT FERRITIC CHROMIUM STEEL

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Heat resistant ferritic chromium steels have inferior creep properties compared to austenitic chromium-nickel steels. But they are used because of their beneficial high temperature corrosion properties especially in case of high sulphur contents in the atmosphere.

One of the major disadvantages of ferritic chromium steels is the loss of strength at relatively low temperatures due to high diffusion coefficients in bcc crystals. For the development of improved creep properties the investigation of the creep mechanisms is necessary. In this paper, the creep mechanisms depending on loading conditions and microstructure were studied.

A ferritic chromium steel was tested in a temperature range of 500 to 750°C and strain rates from  $10^{-6}$  to  $10^{-2}$  s $^{-1}$ . The results indicate, that the creep mechanisms are power law creep in the case of high temperatures and low stresses and exponential creep in the case of low temperatures and high stresses. The transition from one to the other mechanism can be described well by the formula  $k/D_V = 10^{13}$  m $^{-2}$  from Derby and Ashby ( $k$  ... secondary creep rate,  $D_V$  ... lattice diffusion coefficient).

The ferritic chromium steel was tested by samples with two different average grain and carbide sizes and different virgin dislocation microstructures. These two microstructural conditions lead to a different creep behaviour in the lower temperature region whereas the creep behaviour is similar at the higher temperatures. The experiments at higher temperatures (700 and 750°C) indicate that the power law creep is controlled by recovery since the exponent  $n$  is approximately 5 which is typical for this mechanism. Fitting the strain rate against the effective stress an exponent  $n$  about 3 was determined indicating viscous dragging of alloying elements as the dominating creep mechanism. The determination of the internal stress was done by transient dip tests. Problems arising by measuring the internal stresses will be discussed. Furtheron a new modified method of evaluating dip tests will be presented, which allows to eliminate recovery of internal stresses during stress dip.

The results of the creep tests are correlated with electron microscopical investigations of the dislocation microstructure.

MICROALLOYED STEEL FOR HIGH TEMPERATURE SERVICE

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The Czechoslovak metallurgical research in the field of iron and steel industry in cooperation with the producers of boiler steels and of tubes has developed and commissioned the manufacture of new grade of boiler steels with small additions of niobium or vanadium. The technological treatment of these steel grades in the rolling mills, especially manufacture of seamless tubes, makes then use of the latest knowledge on the technology of controlled rolling and cooling. In this respect the steel to ČSN 412025 grade was implemented into the Czechoslovak national standards. The chemical composition of this steel is as follows: 0.14 - 0.20% C; 0.60 - 1.00% Mn; 0.17 - 0.37% Si and some 0.02 - 0.06% Nb or 0.05 - 0.09% V and bal. Fe.

The profound investigation into the substructural characteristics of these steels in the assortment of seamless tubes showed the close relationship among the technological parameters of controlled rolling and cooling of these steel, the dispersity of the precipitating phases and the resultant values of long-term creep strength at elevated temperatures. The reason for markedly enhanced creep resistance of the microalloyed boiler carbon steels consists in high dispersion of the precipitation particles of carbides or carbonitrides of the microalloying elements.

The achieved results showed

- the possible applicability of the Stiefel rolling mills and the Pilger and/or push broaching mills at manufacture of seamless tubes and the applicability of the required regimes of controlled rolling of boiler tubes of microalloyed carbon steels
- the permissible failures in the cadence and frequency of the rolling processes in relation with the thermal strain conditions of controlled rolling and cooling aimed at reaching reasonable reproducibility of the required substructural state to attain a high creep strength,
- the wide economical possibilities of enlargement the field of application of the microalloyed carbon steels at temperatures up to 500°C and their applicability at the temperature intervals in which till now the low-alloyed steels with elevated content of chromium, molybdenum and/or vanadium have been used
- the interest of technically advanced companies and manufactures of the power-generating equipment in such new and economically suitable assortment of rolled products.

THE STRUCTURAL DEGRADATION AND ITS EFFECT ON THE  
MECHANICAL PROPERTIES OF THE 15HM(Cr-Mo) STEEL

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The diagnosis and forecasting of further safe work of parts or installations in power industry is a very complex problem and there are no commonly used and obligatory methods. From amongst many methods used for the assessment of post service properties in power plants and forecasting of its residual life, measuring of fracture toughness and fatigue strength were applied. The results for the Cr-Mo type steels in three structural states, i.e. after standard heat treatment, after a laboratory destabilizing treatment and a simulation of long-term work by heat treatment, and after its exposure for 130.000 and 176.000 h, are shown.

The 15HM steel with tempered martensite and bainitic structure shows the best properties. The initial structure of the specimens revealed pearlite and ferrite grains with some carbide precipitates within the matrix and at the grain boundaries. After a long-term exposure a distinct increase of the ferrite fraction and large oblong carbide precipitations at the grain boundaries were observed. A relatively small difference in fatigue characteristics of the steels investigated is attributed to small structural changes. None of the mechanical parameters studies can serve for univocal assessment of the residual life of the 15HM steel. Structural and creep investigations yield fuller characteristics of the residual life of materials, parts and installations working at elevated temperatures.

The effect of the precipitation behaviour  
on the HAZ-properties of 1 % Cr-Mo-V-steel

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The need of high efficiency power production plants leads to the necessity of better utilisation of the materials used. Beside of base material behaviour the behaviour of the welded component is important to fulfill the requirements of new steam power plants. Recent experiences showed that the weldings are the most weakest part of the component. To receive a better understanding of the cause, mechanism and mass of degradation in welded joints detailed investigations are necessary. By using welding simulation technique (Gleeble 1500) basic studies were performed to investigate the influence of microstructure on toughness, creep, tensile, LCF behaviour and resistance against stress relief cracking of different 1 % CrMoV cast component steels. TEM-investigation on microstructure were carried out using carbon extraction replicas and thin foils. The dissolution, precipitation and deformation behaviour of the heat affected zone was studied as a function of welding parameters, PWHT procedures and service conditions. The results indicate that by using an optimum of chemical composition, appropriate welding technique and PWHT procedure an optimal behaviour of the welded component can be achieved.

VII.5

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Isothermal and Thermomechanical Fatigue Behaviour of the Austenitic  
Stainless Steel 304L Between Room Temperature and 650°C in High Vacuum

poster

withdrawn!

## VII.6

### Creep Fracture in Stabilized Austenitic Stainless Steels

Ryszard H. Kozłowski, Cracow Technocal University, Institute of Materials Science and metal Technology, Cracow, Poland.

One of the most crucial factors limiting the development and the exploitation parameters of creep resistant steels is their susceptibility to brittle fracture, before the creep deformation has attained the admissible value. This phenomenon is also a severe limitation to the use of heat resistant steels in industry. In order to avoid this undesirable effects, chemical composition and microstructure of both existing steels and those being in development, must be optimized.

In this investigation of susceptibility to brittle creep fracture of two austenitic steels H16N13M2 (AISI316) and 00H16N13M2FA steel are presented. In consequence of microalloying of the steels, their creep strength increased and intergranular creep fracture disappeared. Small additions of nitrogen and vanadium to H16N13M2 steel increased its creep strength by some 100%. At 650°C creep strength of the resulting 00H16N13M2FA steel was 180 and 110 MPa for 10 000 and 100 000 hr (extrapolated) creep time, respectively. Theoretical aspects of this work can be utilized for optimization of chemical composition and microstructures of austenitic heat resistant steels, not only of AISI316 type one.

## VII.7

### Relation Between Fracture Toughness and Structural Parameters of High-Strength Microalloyed Steel

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The following pieces of knowledge were drawn from the research into the influence of structure on the fracture toughness of the microalloyed steels X 70 and E 700 under the conditions of the controlled rolling:

Acicular structures are being achieved with the steel E 700 by using the microalloys Mn, Mo, Ti, Zr following the rolling, characterized by a bar-like structure of acicular ferrite which, at a high yield point and ultimate tensile strength, have suitable values of fracture toughness. Nb has a more favourable effect on the uniformity and fineness of structure than Ti.

In all tested steels, by increasing the density of precipitates increasing the yield point can be achieved at the expense of fracture toughness  $K_{IC}$ . It follows from the mathematical relation  $K_{IC} = 82.3 - 17.5 \cdot 10^4 \lambda^{-2}$ , obtained at temperature  $-120^\circ\text{C}$  that in the lowering the interparticle spacing of precipitate from 100 to 60 nm, the value of fracture toughness is lowered by  $30 \text{ MPa m}^{1/2}$ .

From the viewpoint of achieving the necessary level of fracture toughness values it seems requirable that in the process of the controlled rolling and coiling temperatures be low, whereby the lower partial effect of the precipitation effect of steel hardening is achieved, as well as a higher effect of the steel grain hardening.

PRODUCTION OF INTERMETALLIC PHASES BY SOLID STATE  
REACTION OF COLD EXTRUDED ELEMENTAL POWDERS

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A procedure is presented for the production of intermetallic phases from elemental powders. This procedure consists of mainly two parts: Blended elemental powders are cold extruded in order to produce fully dense rods. The rods are then annealed either with or without hydrostatic pressure in order to obtain intermetallic phases. Cold extrusion may be used to produce semifinished products (near net shape). Additionally, the extruded rods can be machined easily in order to produce working parts before forming the intermetallic alloy. Any alloy can be made by this process if the powder mixture is ductile. The range of compositions is only limited by the maximum force of the extrusion press.

Extrusion at room temperature was chosen for two reasons: Firstly, in order to obtain a fine grained intermetallic alloy, reaction time and diffusion paths must be short. This may be obtained by the formation of a fibrous microstructure (fibre composite), where interdiffusion may take place perpendicular to the fibre axis. If the differences in flow stress of the mixed powders are too high, the harder phase does not form fibres during extrusion. Differences in flow stress tend to increase with increasing temperature such that extrusion at low temperatures is essential for the process. Secondly, higher temperatures could lead to uncontrollable reactions between the elements during the extrusion process.

In general, hot isostatic pressing is preferred over simple annealing for the formation process of the intermetallic phase(s). Normally, the interdiffusion coefficients of the different elements are different. During annealing, this leads to the formation of pores, i.e., the Kirkendall effect. A material with large pores is usually unacceptable for mechanical use because of its high brittleness. Hot isostatic pressing leads to a dense material with a decreased brittleness. This is due to the fact that under pressure the formation of pores is hindered and pores may be closed by creep processes.

As a first step, the production of a rod of Ti-36wt.%Al by cold extrusion and subsequent HIP process is shown. This alloy is a two-phase intermetallic compound consisting of the phases  $TiAl$  and  $Ti_3Al$ . The alloy is prepared by mixing the elemental powders and cold extrusion with an extrusion ratio of 14. A 24h simple heat treatment at  $600^{\circ}C$  leads to the above mentioned two phases, but the material has a porosity of 20%. Hot isostatic pressing (1h,  $800^{\circ}C$ ) produces a dense microstructure with good high temperature ductility.



**Grain Boundary Precipitation in Ni<sub>3</sub>Al Based Alloys**

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**Abstract**

Microalloying with boron has been found to give polycrystalline Ni<sub>3</sub>Al alloys, potential superalloy replacement materials, room temperature elongations to failure of up to 50%. However, dynamic oxygen embrittlement along grain boundaries ahead of a crack causes rapid crack propagation in these alloys in the temperature range 600-700°C. Brittle intergranular failure is alleviated to some extent by alloying with chromium, but the mechanism of this improvement is still unclear.

The effect of various alloying elements upon microstructure, particularly at grain boundaries, was investigated for three Ni<sub>3</sub>Al based alloys, Table 1, obtained from Oak Ridge National Laboratory and exposed to a temperature in the range 700-760°C. The microstructure was characterised by transmission electron microscopy (TEM) on a Phillips EM430 and by fine scale EDS/EELS performed on a VG501 FEG/STEM.

In the absence of Cr, alloy 1, a large grain size, 10-25µm, was observed with few anti-phase domain boundaries (APB's). The grain boundaries and dislocations in this alloy were free from precipitation.

The addition of Cr in alloy 2 resulted in a reduction in APB energy as more of these features were observed. The grain size in this alloy was bimodal due to rolling prior to oxidation treatment with large, 5-15µm, recrystallised grains and heavily dislocated subgrains, < 1µm in size. Precipitation of spherical ~50nm diameter particles was observed in grain boundaries in the recrystallised grains and between recrystallised and non-recrystallised regions. EDS analysis revealed these particles to be Cr-rich and selected area diffraction patterns (SADP's) were consistent with Cr<sub>23</sub>(C,B)<sub>6</sub> and Cr<sub>2</sub>B. No precipitation upon the dislocations in the non-recrystallised subgrains was noted.

Alloy 3 had Zr and Ti substituted for Hf and again exhibited APB's, large spherical - 0.5-1.0µm diameter - Cr-rich particles and a bimodal grain structure. Fine subgrains were present, but now the subgrain boundaries were decorated by spherical particles, 30-70nm in diameter. EDS and SADP analysis revealed the precipitates to be based on Cr<sub>2</sub>B and Cr<sub>23</sub>(C,B), but did not indicate increased Zr or Ti contents. EELS on subgrain boundaries suggested the presence of higher B levels, whilst the larger particles gave C and O peaks.

Cr additions cause boride and possibly carbide precipitation on grain boundaries and subgrain boundaries when Zr and Ti are present. Grain boundary enrichment in Ni was observed in all 3 alloys - along with Hf (Alloy 1) and Zr (Alloy 3) - and may be caused by the segregation of B to grain boundaries.

Table 1 Alloy Compositions (at %)

Alloy	Al	Hf	Cr	Zr + Ti	B	Ni
1	22.9	0.5	-	-	0.24	Bal
2	16.8	0.4	8.0	-	0.20	Bal
3	17.1	-	8.0	0.5	0.10	Bal

ON THE ANOMALOUS TEMPERATURE DEPENDENCE OF THE MECHANICAL  
STRENGTH OF  $\text{Ni}_3\text{Al}$

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Many high temperature alloys are strengthened by precipitates of  $\text{Ni}_3\text{Al}$  which have the  $\text{L}_{12}$  crystal structure. These precipitates contain several elements in addition to Ni and Al, but the structure is still that of  $\text{Ni}_3\text{Al}$ . The yield strength of  $\text{Ni}_3\text{Al}$  shows a very anomalous behavior as a function of temperature: it increases as the temperature increases, rather than decreasing, as usual in most alloys. Given the industrial importance of these alloys, it is very important that the strengthening mechanisms which occur in these alloys be understood. Various models have been proposed for several years to explain this anomalous variation. In order to test these models, single crystals of  $\text{Ni}_3\text{Al}(1\%\text{Ta})$  have been deformed in compression together with load relaxation experiments over a range of temperatures. The overall dislocation structure, as well as the detailed core configurations, have been analyzed using weak beam and high resolution TEM techniques.

The macroscopic results show that at a given temperature a normal thermally activated dislocation motion is evidence and as the temperature increases the obstacles get more dense or/and stronger. The TEM observations indicate that at low temperature the majority of dislocations lie on the primary (111) plane with evidence for abundant cross-slip to the  $(\bar{1}\bar{1}1)$  plane. With increasing temperature, this conventional cross-slip process is gradually replaced by the formation straight screw segments which have cross-slipped and completely dissociated on the cross-slip (010) cube plane. The density of dislocations on the cube plane also increases sharply at higher temperatures, even though deformation occurs principally by glide on the primary (111) plane based on slip trace analysis. Weak beam and high resolution observations of dislocation cores also indicate that the antiphase boundary energies on (111) and (010) planes are very similar.

The previously proposed models will be discussed in terms of the new results. They mostly consider that the density of obstacles increases with the temperature, thus causing the anomaly, and do not take into account that a thermally activated motion could be rate controlling. Outlines for a new model are proposed taking into account the above and recent TEM in situ deformation results performed in Toulouse.

## Oxidation and Hot Corrosion Behaviour of Intermetallics

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Intermetallic phases are promising candidate materials for high temperature applications in industrial gas turbines and aero engines. Some of these materials have promising mechanical properties up to very high temperatures. With increasing operation temperature of blade and vane materials the oxidation behaviour becomes more important due to the fact that rapid interdiffusion between coatings and base materials at these temperatures prevent long time operation of coated intermetallic phases. A minimization of oxidation rates as well as optimization of oxide scale adherence by addition of some alloying elements to intermetallic phases is very important to improve their oxidation resistance. Furthermore evaporation of oxides may result in rapid degradation of such components.

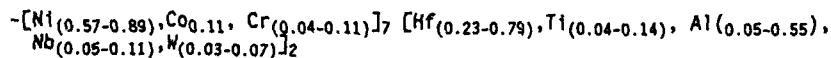
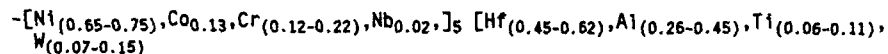
The paper describes some fundamentals of evaporation of  $\text{Cr}_2\text{O}_3$ -,  $\text{Al}_2\text{O}_3$ - and  $\text{SiO}_2$ -scales at temperatures higher than  $900^\circ\text{C}$ . Results of oxidation and hot corrosion measurements of different types of intermetallic phases ( $\text{NiAl}$ -,  $\text{NbAl}_3$ -,  $\text{TiCr}_2$ -,  $\text{Ti-Al-Si}$  and some silicides) are presented, which show the potential of these systems for high temperature applications and the limits of their temperature capability.

Electron Microprobe Investigation of Lower Melting Regions in As-cast Structure of DS200 + Hf Single Crystal

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Data obtained using electron microprobe techniques have allowed the incipient melting (or lower melting) regions in the as-cast condition of DS200 + Hf single crystal to be studied. The large variability of composition was observed in the incipient melting regions. For example, Ni and Hf contents vary between 27.35-59.94 wt.%, 14.47-54.87 wt.%, respectively. This investigation indicated that, in addition to the  $\text{Ni}_5\text{Hf}$  type compound, the  $\text{Ni}_7\text{Hf}_2$  type intermetallic phase exists in the incipient melting regions. Both  $\text{Ni}_5\text{Hf}$  and  $\text{Ni}_7\text{Hf}_2$  show considerable solubilities for Cr, Co and Al. In  $\text{Ni}_7\text{Hf}_2$  the Ni is replaced by Co and Cr elements. The maximum solubility observed for these elements are ~8 at% for Co, ~10 at% for Cr and ~12 at% for Al. The considerable solubilities of Cr (max.14 at%), Co (max.12 at%) and Al (max.~6 at%) were also observed in the  $\text{Ni}_5\text{Hf}$  compound. However the solubilities of W, Ti and Nb were not appreciable in these compounds. From the analyses performed on the incipient melting regions the  $\text{Ni}_5\text{Hf}$  and  $\text{Ni}_7\text{Hf}_2$  type compounds have the following stoichiometric formula in the DS200 + Hf alloy:



The incipient melting regions always occur in the vicinity of the rosette type ( $\gamma + \gamma'$ ) eutectic pools. Usually there are (Hf, Nb)C type carbide particles which are connected to or very close to the incipient melting regions.

**Phase Diagrams of the  
Ni-Fe-Mo and Ni-Cr-Mo Ternary Systems  
Experiments and Thermodynamic Calculations  
as a Basis of Superalloy Development**

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For both systems specimen of various compositions were melted and then aged at 1473, 1273, 1123 and 973 K respectively. The phases and their compositions have been analysed by SEM, EDS and X-ray diffraction analysis. The maximum solubility range of the solid solution  $\gamma$  phase as well as the concentrations of the intermetallic TCP phases were determined. The liquidus and solidus temperatures were measured by DTA.

The ternary systems were thermodynamically calculated on the base of the available SGTE Gibbs functions for the phases of the binary edge systems, using the computer program "PMLFKT". In these calculations the intermetallic phases were described by the sublattice model.

Isothermal, as well as T-c sections of the ternary systems were calculated and compared with the experimental values. Now coefficients were introduced into the thermodynamic descriptions of the  $\sigma$ -,  $\mu$ - and P-phases of the binary Mo-Ni system, where these phases are not stable, as well as ternary coefficients. In repeated calculations, these coefficients were systematically changed, until the calculated diagrams fitted sufficiently well to the experimental points.

For the quaternary Ni-Fe-Mo-Cr system some preliminary calculations were performed.

## Pseudo ternary systems as models to explain the metallurgical structure of superalloys

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The constitutional effects of alloying additions in superalloys are complex and involve many aspects. The promotion of  $\gamma'$  precipitates is the main requirement in order to improve high temperature and microstructural stability. The role of titanium as  $\gamma'$  stabilizer is well known and it is shared in more recent alloys with tantalum for instance.

Model alloys systems were chosen for their ability to illustrate competing elements in the formation of A3B phases i.e. aluminium and titanium ; aluminium and tantalum. A solid solution was substituted for nickel in the pseudoternary systems "S"-Al-Ti and "S"-Al-Ta. The range of compositions of the primary solidification phases was determined in order to observe the changes due to the elements present in the solid solution.

Particular attention was focused on the phase equilibria involving  $\gamma'$  with high content of titanium or tantalum. In the case of system with titanium, a metastable  $L1_2$  phase may form with a composition close to  $Ni_3Ti$ . In the case of system with tantalum, another metastable phase  $\gamma''$ , with a  $DO_{22}$  structure and a composition close to  $Ni_3Ta$ , was detected. The occurrence of these phases in complex alloys will be discussed by comparison with ternary model alloys.

**Microscopic Structural Study of NiCrAl Ternary System****Dr. L.B.Hussain****University of Technology  
School of Applied Science**

A variety of chemical composition of NiCrAl can be produced by co-sputtering using a modified planar magnetron sputtering deposition system, consisting of high purity Nickel, Chromium and Aluminum segmented target allows the deposition of a range of NiCrAl thin coating compositions within one deposition trial. Assessment of phase structures using Transmission Electron Microscope which two distinct areas are observed on results in ring diffraction pattern (the amorphous phase) while the second produces a distinct spotty pattern (the crystalline phase). Growth of these phase and the change in structure of NiCrAl coating have been investigated by the heat treatment of samples using a hot stage on the Transmission Electron Microscope. Short exposure under 2 hr, structural changes were observed as the temperature increased up to 750 °C permit the phase diagram of NiCrAl alloys to be established up to 44 wt% Al and 58 wt% Cr.

## THE STUDY OF DISTRIBUTION COEFFICIENT OF TUNGSTEN IN TANTALUM

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An important characteristic of the process of purifying high melting metals by crystallization is the distribution coefficient  $k$ , representing the ratio of the impurity concentration in the solid and liquid phases. Since the refining is applied to almost pure metal, it is of interest to consider the limit portion of the phase diagram.

From known thermodynamic data the value of  $k$  of tungsten in tantalum was calculated by Kaufman method yielding  $k = 1$  and showing the possibility of existence of a minimum at 3.7 mol.% and 3271 K. The value of  $k$  was also calculated from known phase diagram experimentally constructed by Savitski ( $k = 1.08$ ).

The experimental value of  $k$  was determined by electron beam zone melting of tantalum at high vacuum by method of frozen zone and neutron activation analysis. For some speeds of zone it is found that  $k \geq 1$ , whereas for some other speeds  $k \leq 1$ . The theoretical results obtained by Kaufmann method are in good agreement with experimental values.



The Beneficial Effect of Reactive Elements on the Oxidation Behaviour of  
Alumina-Forming Materials at High Temperature - A Review

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The current viewpoints concerning the explanation of the beneficial influence of small amounts of certain reactive elements such as Y, Ce, La, and Hf on the oxidation behaviour of alumina-forming materials at high temperature (above 1270 K) are briefly reviewed.

In particular, the role of reactive elements in the neutralization of the detrimental effect of trace impurities (S, P, Cl, ...) and in the relief of the stresses generated in the scale-substrate system during oxidation is considered. The influence of reactive element dopants on the transport properties of the alumina scale is discussed against the background of diffusion data available in the literature.

In conclusion, it is supposed that a number of individual effects contribute to the overall beneficial influence, whose relative efficiencies depend on various factors, such as: the alloy composition, its microstructure, the reaction conditions, and the type of reactive element as well as the form of its presence in the substrate.

The directions of necessary further investigations are suggested.

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\* On leave from the Institute of Materials Science, Academy of Mining and Metallurgy, Kraków, Poland

Effect of Variouslly Processed NiCoCrAlY Coatings  
on Microstructure and on Hot Corrosion Resistance

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A comparative study of NiCoCrAlY overlay coatings on CMSX-2 Ni-base superalloy single crystals was performed with samples processed by three different coating techniques, i.e., (a) EB-PVD (Electron Beam Physical Vapor Deposition), (b) LPPS (Low Pressure Plasma Spraying), and (c) High rate ion plating.

Since the coating layers processed by EB-PVD and LPPS technique contained relatively high amounts of pores, glass-ball shot-peening and annealing processes were additionally applied to improve the density of the coating layers. Coating layer processed by high rate ion plating exhibited even and sound microstructure.

Transverse sectional microstructure and microchemistry of the differently processed coating layers were investigated by STEM techniques. Due to the variety of coating procedures utilized, bonding between matrix and coating layer, grain size, growth phenomena, porosity, beta to gamma phase ratio and their lattice parameters, twin band width and amount, occurrence of metastable phases in the NiCoCrAlY coating layer exhibited varieties. These are representative for their respective degree of thermodynamic stability.

Hot corrosion and oxidation properties of the differently processed NiCoCrAlY coatings were evaluated by burner rig testing. The respective hot corrosion resistance of the layers was determined by gravimetry, metallography and SEM. A ranking of hot corrosion resistance of the differently processed samples was attempted. This ranking of properties can be attributed to the respective degree of thermodynamic stability of the microstructure.

*The Effect of Reactive Elements on the High-Temperature-Oxidation  
Behaviour of Ferritic FeCrAl Alloys*

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The gradual modification of the composition of a Fe-23Cr-5Al-0.2Zr ferritic alloy of commercial purity by addition of reactive elements in different forms made the comparison of their efficiency in improving the oxidation behaviour of the material under study possible. The reactive elements have been added as the natural mixture of their oxides (so-called: *mischmetall*), as elemental yttrium and hafnium, and as implanted yttrium.

The oxidation has been carried out in the temperature range 1573 to 1623 K. under isothermal and thermal cycling conditions, in oxygen and in air, respectively. The microstructure and morphology of the starting materials as well as of the scales have been studied using optical and scanning electron microscopy. The composition of the alloys and the scales has been determined by means of various X-ray techniques.

The dependence of the efficiency of reactive element additions on the form of their presence in the alloy as well as on the substrate microstructure has been established. The influence of implanted yttrium decreased with increasing purity of the starting material.

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<sup>+</sup> On leave from the Institute of Materials Science, Academy of Mining and Metallurgy, Kraków, Poland.

A MODEL TO PREDICT OXIDIZING - CARBURIZING RESISTANCE  
OF AUSTENITIC STAINLESS STEELS AS A FUNCTION OF  
ALLOY CHEMISTRY

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A computer program has been used in order to describe and accurately determine the resistance of a wide range of austenitic stainless steels in a  $H_2$ -CO-CO<sub>2</sub>-H<sub>2</sub>O (Cp = 0.9%) atmosphere as a function of alloy chemistry.

The alloy's resistance has been assessed by using three different criteria :

- i) mass pickup,
- ii) diffusion coefficient of carbon, and
- iii) depth of carburized layer

The functional relationship between chemical composition and alloy's resistance has been described with the second order regression analysis method.

Based on this model it has been found that the alloys consisting of 18% Cr - 34% Ni, 26% Cr - 26% Ni - 0.17% C and 22% Cr - 27% Ni exhibit minimum mass pickup, maximum resistance to carbon diffusion and minimum depth of carburized layer respectively.

Study of Insulation Layer Formation on Electrical Steel Surfaces by X-ray Photoelectron Spectroscopy and Electron Microprobe Analysis

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By means of X-ray photoelectron spectroscopy (XPS) and electron microprobe analysis (EMA) the formation of the insulation layer on grain oriented Fe-3%Si electrical steel was studied. This insulation layer is developed by three processing steps:

- oxide layer formation during decarburization annealing
- formation of "glass-film" during box annealing
- phosphate coating during stress relief annealing

The essential properties of the insulation layer like adhesion and oxidation resistance depend on the structure of the glass-film. It is formed by the reaction of magnesium oxide with the oxide layer to magnesium iron silicate.

XPS in combination with Ar ion sputtering was applied to determine qualitative elemental concentration profiles across the oxide layer with a fair depth resolution ( $< 100$  nm for homogeneous layers). By measuring the "chemical shift" of the XPS-signal informations about the chemical structure of the formed oxides were obtained. This was used to distinguish between  $\text{Fe}^0/\text{Fe}^{2+}$  and  $\text{Si}^0/\text{Si}^{4+}$ , respectively, and allowed to locate the depth of the interface between metallic iron and iron oxide.

EMA was applied to determine quantitative elemental concentration profiles by analyzing embedded and polished cross-sections. The resolution of EMA is limited to about  $2 \mu\text{m}$  and was consequently applied only to the analysis of the thicker glass-film.

X.6

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Burner Rig Tests of EB-PVD Coatings on DSE  $\gamma/\gamma'$ - $\alpha$

poster

withdrawn!

NEW METALLIC FELTS  
WITH IMPROVED RESISTANCE TO HIGH TEMPERATURE OXIDATION

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The fabrication of metallic felts with coarse fibres (a few tens of micrometers for thickness or diameter) is industrially performed, either by cold clawing (steel wool) or by wire drawing. In both cases, the materials which are used must possess adapted properties to these processes. Particularly, they must be sufficiently ductile to give either long chips or wires with a section generally circular. This condition limits the fibres composition to moderately strengthened alloys. In the case of MCrAlY alloys ( $M = Ni, Co, Fe$ ), which are used for the turbine blades coating, the aluminum content which controls the oxidation resistance is, for some compositions, too high for the ductility needed by these techniques; even if, for some of these alloys, a severe control of the process parameters allows to apply these techniques, the cost remains high.

ONERA, which developed the elaboration of MCrAlY ribbons by melt-spinning for honeycombs fabrication with improved resistance to high temperature oxidation, applied this process to the fabrication of fibres. As for ribbons, the use of melt-spinning leads to a simpler process which is reduced to the casting of the alloy.

The fibres which are obtained directly from the melted alloy are like very thin chips, with a semi-circular section. The width and the thickness can be easily controlled. The length varies from a few centimeters to several tens of centimeters and can be possibly shortened by crushing, which in addition allows to twist the fibres.

A felt is obtained by a controlled atmosphere sintering, the porosity being easily reduced by pressing.

The oxidation resistance of these materials is very good up to 1150°C and is reasonable up to 1250°C for a short time.

These felts, which were originally conceived for turboengine abradable seals, find applications in catalytic exhaust for motor vehicle or as dust filters at high temperature.

Microstructural Aspects of Processing of Sintered SiC  
and Si<sub>3</sub>N<sub>4</sub>

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Sintered SiC and Si<sub>3</sub>N<sub>4</sub> are the most interesting high performance ceramic materials due to their potential for low as well as high temperature applications. The difficulties encountered in the pressureless densification of SiC and Si<sub>3</sub>N<sub>4</sub> are common to covalent ceramics. The difficulties can be overcome by applying high pressure or by adding different types and amounts of densification aids. Both the additives and impurity elements of the raw materials can strongly influence manifold properties, while the high temperature behaviour of these types of ceramics is largely controlled by the presence and nature of second phases. In order to understand these influences, the raw materials have been investigated regarding grain size and grain form, specific surface area and content of O and impurity elements. At fixed conditions, the effect of different types of powder has been studied using constant amounts of B and C as additives for SiC and Y<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> for Si<sub>3</sub>N<sub>4</sub>, resp. The conditioned powders have been isostatically pressed and sintered.

The aim of this investigation is to discuss the effects of processing on the microstructural development of sintered SiC and Si<sub>3</sub>N<sub>4</sub>. Correlations between the materials properties and microstructural aspects are given.



PHYSICAL PROPERTIES AND FRACTURE MECHANICS  
OF PRESSURELESS SINTERED SiC

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A commercially produced, pressureless sintered, monolithic SiC containing 0.5 wt.% B and 3.8 wt.% phenolresin was investigated in order to develop a consistent data base for design applications. The elastic constants, the linear expansion coefficient, the thermal conductivity, the fracture toughness, the bending strength, the oxidation behaviour and the creep properties were measured up to 1673 K. Bending tests at low stress rates did not show any effect from subcritical crack growth. Tensile tests on specimens with a large volume were performed at room temperature. Weibull theory was used to explain the volume dependence of strength. This data base was used to predict the thermal shock behaviour of the material. The theoretical analysis showed excellent agreement with experimental tests made on small penny like disks heated by halogen lamps.

# INJECTION MOULDING OF ALUMINA

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The principles of ceramic injection moulding have been studied in TUT/Institute of Plastics Technology for about three years. The ceramic powder been used is reactive alumina CT 3000 SG (Alcoa). Originally, two different binder systems, one based on paraffin wax and the other based on acrylic resin, have been examined. Later on new formulations have been made suitable for injection moulding. Mixing has been made with a torque rheometer and with a larger patch type kneader. Injection moulding parameters have been studied with both plunger type and screw type injection moulding machines.

The research has been made in cooperation with Helsinki University of Technology, where debinding conditions and sintering temperatures have been investigated. The fracture strength of the sintered parts has been measured by 4-point bending tests. Also the microstructure of fracture surface and surface roughness of the sintered specimens have been studied.

The aim of this research has been to find the optimal injection moulding parameters for the two binder systems and to make defect free pieces. Further aims are to develop new binder systems and to study the mixing procedure.

On Hot Pressing of Hexagonal Boron Nitride

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Changes of chemical composition, crystallites size and apparent density occurring during hot pressing of boron nitride are discussed in this paper to suggest a model of this process.

It has been noticed in the very beginning that size of boron nitride crystallites does not depend on external pressure, but it depends on sintering temperature, above all. On the other hand, very close correspondence between apparent density of sintered material and the size of the crystallites has been found, when pressure of sintering affects kinetics of the process. Key temperature, given by maximum rate of the crystallites growth and the rising of density of sintered body, was found to lie between 1350° and 1450° C. Outstanding changes of chemical composition were found at the same temperature range. Both these phenomena are individually connected each to other, and they are accompanied with rising of crystallites mobility, leading to mass re-distribution in hot-pressed material.

All these facts together with the results of chemism analysis of both synthesis and pressure sintering of boron nitride being originally turbostratic allow this process to qualify as a condensation polymerization, which is accompanied with boron oxide and water releasing. At the same time, when planary macromolecules of boron nitride grow, ceramic skeleton forms as a result of intergranular coalescence of the crystallites. This phenomenon is conditioned by overpowering of surface barrier between neighbouring granulas by means of external pressure. Thus, particular monocrystal zones (crystallites) loose their identity and probability of intergranular coalescence becomes equal to probability of intragranular one.

Finally, sintering potential of hexagonal boron nitride is allowed to be qualified as a combination of two independent contributions: the difference between surface energy of granulas and external pressure on the one hand, and the difference between the structural parameters of both starting and final materials (size of crystallites, for example) on the other hand. As the latter difference can be controlled over degree of initial powder turbostraticity, amorphous preparatives with poorly developed crystal lattice and with small monocrystal zones are the most suitable initial materials for obtaining pore-free ceramics.

Simulation models for studying properties  
of composite materials manufactured by thermal spraying processes  
of ceramic-powders

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Thermally-sprayed coatings are used in many fields of engineering to protect components against wear, corrosion and thermal load. The required properties of coatings are closely dependent on their typical structural characteristics and the resulting material data.

The structure of thermally-sprayed coatings is principally characterized by its lamellar nature and its more or less high porosity. The lamellar structure is created by impacting of molten or highly plastic particles on the substrate surface or on the already existing coating; the porosity is the result of contraction during solidification of the particles, of other fit problems or of dissolved gases.

The process by which discrete molten particles impact arbitrary points within a surface area can be simulated using the Monte-Carlo method. An appropriate calculational model is presented. The impact velocity and the physical data of the spray particles at the moment of impact serve as simulation input data. Results by varying input data are presented graphically as cross sections of the coatings and are compared with real coatings.

These results are the basis for further modelling as for example the calculation of temperature curves in the coating and substrate during the spraying process and at the end of the process. These curves are of great interest to study the built up of thermal stresses. Time and local dependent temperature curves for  $Al_2O_3$  and Ta on austenite and ferrite are presented and discussed.

XI.6

W. Huettnner, R. Weiss, Schunk Kohlenstofftechnik GmbH, Gießen (FRG)

Oxidation Inhibited Carbon/Carbon: a Candidate Material for Hot Structures

poster  
withdrawn!

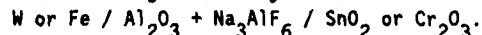
PREPARATION AND TESTING OF CERAMIC PROBES ( $\text{SnO}_2$  AND  $\text{Cr}_2\text{O}_3$ ) FOR THE MEASUREMENT OF  $\text{Al}_2\text{O}_3$  CONCENTRATION IN ELECTROLYTIC ALUMINIUM CELL

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The measurement of alumina concentration in electrolytic aluminium cells is still affected by the lack of wholly reliable experimental equipments.

When the amount of alumina in the electrolytic cell becomes approximately as low as 1.5 %, an "anode effect" takes place. The appearance of the anode effect does not allow the cell to be still operated properly: in order to maintain the normal amperage, the voltage required ranges up to ten times greater than the normal operating voltage.

The majority of papers and patents cited in the open literature are concerned with indirect measurements of content of alumina based upon voltage / resistance of the cell; direct measurements are mainly affected by limited resistance of probe materials in fused cryolytic bath. The state of the art of direct measurements was critically evaluated and a couple of oxide ceramics ( $\text{SnO}_2$  and  $\text{Cr}_2\text{O}_3$ ), particularly resistant to the cryolytic bath was selected for experimental testing. The preparation of  $\text{SnO}_2$  and  $\text{Cr}_2\text{O}_3$  probes, as well as the results of an experimentation<sup>2</sup> carried out with both electrodes each coupled with two metallic electrodes (Fe or W) are described. The alumina concentration is measured through the e.m.f. generated by the cell:



This study was developed in connection with a contract between Aluminia Spa and ENEA.

XI.8

F. Castro, I. Iturriza, J. Echeberria, Centro de Estudios e Investigaciones Tecnicas de Guipuzcoa, San Sebastian (Spain)

Glass Powder Encapsulation and Hipping of Silicon Nitride Ceramics

poster  
withdrawn!

# COMPUTER-BASED MODELLING AND SOLUTION PROCESSING OF POWDER MATERIALS.

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Solution processing, e.g. coprecipitation, of composite materials has several advantages, especially for large scale production. The processing can be carried out in aqueous or non-aqueous systems with a great variety of complexing reagents (ligands) to form the precursors for powder products. However, effective use of this technique requires a precise knowledge and exact modelling of all the chemical equilibria involved for a given set of conditions.

In this paper, we report some examples for synthesis of high temperature superconducting ceramics. Computer-based modelling of reaction equilibria has been used to simulate the operating conditions required for preparation of Y-, Bi- and Ti-based composite precursors. The operational criteria of these processes have been systematically investigated by modelling the respective systems with available data base. The different equilibria involved were characterized and the corresponding reaction constants were calculated for relevant conditions under which the powder can be obtained with a given compositions. Fig. 1 shows a typical calculation results for the carbonate coprecipitation of BiPbSrCaCu precursor. Fig. 2 shows a typical curve of particle size distribution for oxalate powder of Bi-based precursor. The computer simulation has greatly simplified the experimental work needed to ascertain the optimum operating conditions. On the other hand, a computer controlled laboratory unit for solution processing is constructed and used for verifying the preparation performance under various operating conditions. For the extensive criteria of computer-aided solution processing, the stoichiometry, purity and homogeneity of both the bulk specimen and individual particles have been examined by different experimental techniques. The particle morphology and crystallinity of these materials have been also studied.

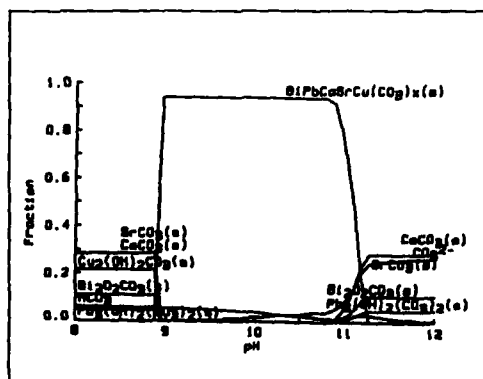


Figure 1. Modelling of Powder Formation

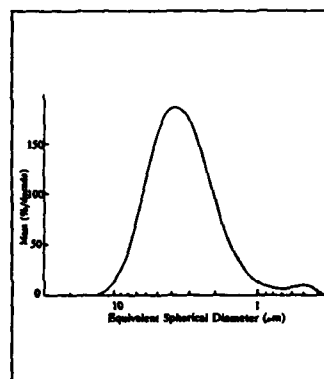


Figure 2. Particle Distribution



A High Temperature Bi-Sr-Ca-Cu-O Superconducting Phase

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A high temperature superconducting phase of the nominally  $\text{Bi}_4\text{Sr}_{2.5}\text{Ca}_{2.5}\text{Cu}_4\text{O}_x$  compound has been prepared by the solid state reaction method with a  $T_c = 80\text{K}$ . X-ray diffraction studies show mainly one phase, which can be indexed on the basis of a tetragonal unit cell, with the indicative presence of other phases. Optical examination in reflected light indicates the presence of three phases with characteristic optical properties, one of them being the major. Electron microprobe analysis shows that the major phase contains all four cations in the proportions  $\text{Bi}:\text{Sr}:\text{Ca}:\text{Cu} = 4.66:2.72:2.66:4$ , while the other two are  $\text{CuO}$  and  $\text{Ca}_2\text{CuO}_3$ . Electron paramagnetic resonance (EPR) spectroscopy gives, at temperatures above  $T_c$ , a strong signal which is attributed to  $\text{Cu}^{2+}$  ions with tetragonal local symmetry. The calculated spin-Hamiltonian parameters are  $g_1 = 2.373(5)$  and  $g_2 = 2.214(5)$ . A comparison is made between the local symmetry of the  $\text{Cu}^{2+}$  ions complexes in our Bi sample and in the Y-Ba-Cu-O superconductor studied by us previously.

GLASS-CERAMIC AND CERAMIC MATERIALS  
IN THE Bi-Ca-Sr-Cu-O AND Bi-Ca-Sr-Cu-Pb-O SYSTEMS

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The glass-formation for compositions of the Bi-Ca-Sr-Cu-O and Bi-Ca-Sr-Cu-Pb-O systems with different content of  $\text{Bi}_2\text{O}_3$  was investigated. Using DTA and TEM it was found that stable glasses without crystalline impurities could be prepared by a twin roller quenching method. The addition of PbO stimulates the glass-formation and decreases the temperature of synthesis. For the more glass-compositions the glass-transition and softening points vary from  $390^\circ\text{C}$  to  $500^\circ\text{C}$ .

Glass-ceramic and ceramic materials were obtained by appropriate thermal treatment. The crystal phases obtained in this way are responsible for high-temperature superconductivity of the materials.

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MICROSTRUCTURE AND PHASE-FORMATION OF CERAMIC MATERIAL  
IN Nd-Ba-Cu-Ag-O SYSTEM

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The elements' and phases' distribution as well as the micro-morphology of ceramic material in the Nd-Ba-Cu-Ag-O system were investigated by means of electron probe microanalysis, X-ray diffraction, scanning electron microscopy and IR-spectroscopy.

Comparison with Y-Ba-Cu-Ag-O ceramic material was made.

In the both systems the introduction of silver leads to the formation of multiphase structures. The ceramic materials with participation of neodymium show more uniform micro-structure.

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Supported by Bulgarian Committee of Science, Contract N 705, 1988

Influence of Heat Treatment on Microstructure and Properties  
of an Advanced High Temperature Titanium Alloy

M.A. Däubler, MTU München, speaker

M.T. Cope, Rolls Royce, Derby

In order to improve the efficiency and performance of gas turbine engines, advanced materials are required which possess increased strength, lower density and higher temperature capability compared to current alloys. IMI 834, a near  $\alpha$  titanium alloy, is the latest development in a family of materials that have extended envisaged component operation temperatures to 600 °C.

Previous alloys including IMI 685 and IMI 829 were heat treated above the beta transus to coarsen the structure and improve creep resistance. In order to refine the structure and improve strength, IMI 834 is heat treated high in the alpha and beta phase field which results in a prior beta grain size of less than 1 mm. Alloy chemistry modifications were made to IMI 834 to maintain a creep benefit over previous near  $\alpha$  alloys despite the finer microstructure.

This paper presents results of a range of studies which explore the influences of solution treatment, quench rate and ageing parameters on the balance of mechanical properties.

PHASE TRANSFORMATIONS IN Ti-Al-C ALLOYS

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Commercially produced Ti-Al based near- $\alpha$  alloys are used extensively in the aerospace industry at temperatures up to 600°C. Despite their brittleness at room temperature, the titanium aluminides,  $Ti_3Al$  ( $\alpha_2$ ) and  $TiAl$  ( $\gamma$ ) combine relatively lower densities with good high temperature strength, and with oxidation resistance up to ~650°C and ~1000°C respectively. These compounds are attracting extensive interest as potential future aerospace structural materials to replace near- $\alpha$  and nickel based alloys. Alternatively, titanium metal matrix composites could be developed by reinforcing the Ti-alloy with rare earth oxides, SiC or TiC. In either case the phase equilibria and transformations involved must be established.

In the work to be reported, various carbon additions (1.0 to 3.0 at % C) were made to Ti-Al based alloys, containing 15 to 55 at % Al. Heat-treatments were given involving quenching from 1250°C and annealing for various times at selected temperatures in the range of 1050-450°C; a particular objective was to determine the potential for achieving strengthening by carbide precipitation from supersaturated solid solution. The microstructures were studied by optical, scanning and transmission electron microscopy, x-ray diffraction, and x-ray ED spectroscopy.

Three compounds were present in the range of compositions studied, namely TiC,  $Ti_3AlC$  (P-phase), and  $Ti_2AlC$  (H-phase). In the alloys of higher aluminium content (26 and 55 at % Al) the carbide phases encountered were  $Ti_3AlC$  and  $Ti_2AlC$  respectively. No significant carbide precipitation was obtained on ageing in the  $\alpha_2$  or  $\gamma$  + carbide phase fields, indicating no significant solubility differences as a function of temperature. At lower aluminium content (15 at % Al), TiC is present in equilibrium with  $\beta$ -phase at 1250°C and enters into solid solution in  $\alpha$ -phase at 1050°C showing significant increase in the solubility of C with the change in matrix crystal structure. Ageing at lower temperatures resulted in precipitation of dispersions of TiC, demonstrating a decreasing C solubility with decreasing temperature. Some age hardening can thereby be obtained.

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## The Preparation of Ti-based Metal Matrix Composites Via a Casting Route

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The current solid state methods of producing Ti-metal matrix composites are very expensive. In an attempt to reduce the costs of such materials, experiments are underway to assess the feasibility of producing Ti composites via a casting route. Preliminary work has shown that one possibility is to use TiC as the reinforcement addition and the present work reports on the current state of this programme. Cast Ti/TiC composites have been prepared and tested at room temperature in tension to determine the basic mechanical properties and the mode of failure. The results showed that there was a substantial increase in stiffness and strength but that the ductility was significantly reduced. Scanning electron microscopy (SEM) has shown that failure occurs by cracks initiating in the TiC particulate.

Further work is underway in which the processing parameters will be changed in order to control the size and distribution of the TiC. These samples will be tested at room and elevated temperatures and again examined after failure using SEM in order to assess the factors which give rise to any changes in properties. These results will be presented together with calculations which allow the change in the elastic properties to be predicted for particulate additions.

**SUBSTRUCTURE DEVELOPED IN THE HOT WORKING  
OF Al-Li ALLOYS**

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The substructure behaviour of two Al-Li-Cu-Mg-Zr alloys has been studied in order to determine the microscopic mechanisms which control the superplastic behaviour. The alloys were deformed in torsion at 300-500°C and strain rate  $0.1-4 \text{ s}^{-1}$  up to equivalent strains of 4.

The alloys were deformed in two conditions: 1. Solution treated at 546°C, then cooled to test temperature; 2. Overaged 8 hours at 400°C. The flow stresses were found to depend on the strain rate through a sinh function with exponent 3.1 and 3.5 and on temperature through Arrhenius term with activation energies 209 and 185 kJ/mol.

The subgrain sizes, spacing of dislocation composing subgrain boundaries and angle of misorientation across the subgrain boundaries were determined. The interaction of dislocation with solute or dispersoids are analyzed.

In additional tests, for overaged alloys, the hot working strain rates were abruptly changed to values  $10^{-5}-10^{-3} \text{ s}^{-1}$ , followed by measurement of strain rate sensitivity in order to investigate the superplastic behaviour. The microstructure after superplastic experiments are analyzed.

Effect of Casting Parameters and Heat Treatment  
on the Properties of an Investment Cast  
Al-7Si-4Cu Alloy Component

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An aerospace precision, initially forged, component consisting of thick and thin sections with compound angles has been successfully produced by investment casting of Al-7Si-4Cu alloy. The cooling curves of the mould and cast metal have been prepared. The quality and mechanical properties including the specific strength of the component have been optimized through appropriate combination of processing parameters i.e mould temperature, melt temperature at the time of pouring and the time of opening mould after solidification.

Porosity, grain size and distortion produced in the castings have been plotted as functions of processing parameters. Distortion caused due to post-casting solution treatment at 520°C for 3 hours with subsequent water quenching and aging has been measured. Recommendations also given for proper heat treatment of the precision cast component.

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**The Effect of the Matrix-Reinforcement Interface on the Ageing Response of an Aluminium 6061 Alloy Reinforced with 20 vol % SiC Particulates**

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Metal matrix composites (MMC's) offer the possibility of substantially increasing the stiffness and strength of various alloys in a similar manner to polymer based composites, but at greater operating temperatures. Currently, commercial alloys are used as matrices in aluminium based MMC's and the composites are heat treated using standard schedules for those alloys, without optimising for the introduction of the matrix-reinforcement interface.

The effect of the matrix-reinforcement interface on microstructural development and mechanical properties of an Al(6061)-20vol% SiC<sub>p</sub> composite was investigated using TEM, STEM, AES, microhardness and miniature tensile testing. Both reinforced and unreinforced alloy samples were solution treated for 2 hrs at 530°C then aged in the temperature range 120-230°C for 1-1000 hrs, Table 1.

Microanalysis revealed Mg and Si segregation to the SiC/Al interface prior to precipitation in the bulk or at the interface, Figure 1. On ageing, segregation promoted formation of a band of Mg<sub>2</sub>Si at the SiC/Al interface, Figure 2, which depleted the remaining matrix in solute. The presence of the reinforcement also caused thermal mismatch dislocations to be punched out on cooling. This gave rise to an increase in the density of nucleation sites for  $\beta'$  MgAl precipitates, resulting in an acceleration in ageing kinetics compared with the unreinforced alloy at 170 and 230°C. The SiC/Al interface acts as a sink for vacancies and so zone formation at 120°C was suppressed in the reinforced alloy, but still occurred in the unreinforced alloy. In the latter, the matrix was not depleted in Mg and Si to the same extent as the reinforced alloy and Mg<sub>2</sub>Si precipitates formed in addition to MgAl.

The presence of the reinforcement caused ageing kinetics to be accelerated, but the total extent was reduced. The development of matrix hardness was therefore faster, but less pronounced than in comparable unreinforced alloy, Tables 2, Figure 3.

The presence of the reinforcement also caused a large decrease in reduction in area (RA) to failure, Figure 4. Failure in both alloys took place by ductile matrix rupture around matrix precipitates with some cleavage of large SiC particles; interfacial decohesion was rare. Ageing, and hence matrix precipitate population, had little effect on the RA of the reinforced alloy. This is explained by the dominant influence of large, cracked SiC particles giving rise to strain concentration, shear band formation and, during ageing, possible shielding of the matrix by the formation of interfacial Mg<sub>2</sub>Si.

High-Strength Wrought Al-Zn-Mg-Cu Alloys for Aeronautical Applications

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We are investigating a series of high-strength wrought Al-alloys, on the basis of Al-Zn-Mg-Cu system, with Cr, Mn, Ni, Ti, B, Zr for aircraft propeller, blades, frames for very high strength 600 - 700 MPa. The total amount of Zn % + Mg % + Cu % control the properties and consequently the uses. When the total is above 9 % high strength is paramount and formability, weldability and corrosion resistance are subordinated to it. All these alloys are age hardenable, but the intermetallic compounds are different. We are investigating the influence of non-metallic and metallic impurities, the action of modifiers, the direct and inverse segregations and the mechanical properties depending of temperatures and times of homogenisation, solution treatment and age hardening. The thermomechanical treatment are considered as more effective.  
Results of experiment are presented.

Properties of Consolidated Magnesium Alloy Powder

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New developments in inert gas atomisation and improvements in mechanical preparation of powder have opened new opportunities for magnesium alloys. It is possible to consolidate magnesium alloy powders and produce fine grain material with a homogeneous distribution of fine precipitates. These contribute to a good range of properties. A further improvement can be achieved by selected alloy development as was the case for aluminium alloys when rapid quenching technology was applied.

Different commercially available magnesium alloys were converted to powder by inert gas atomisation and mechanical methods. The alloy used (AZ91, MSR, QE21 and ZE63) are a medium strength, two high temperature and a high strength alloy respectively which are usually used for sand, ingot or pressing casting. The powders were characterised and the powder properties determined as a function of production parameters. The consolidation of such powder into useable solid magnesium necessitate appropriate techniques. The influence of the powder production on the final properties is discussed and these are compared with those of conventionally produced alloys. Properties of consolidated powders are influenced by the proportion of oxides, oxide distribution, grain size and condition of deformation.

Hardness and tensile strength were determined at room and elevated temperatures and correlated with the microstructure.

## ELECTRICAL PROPERTIES OF RAPIDLY SOLIDIFIED Cu-Cr ALLOYS

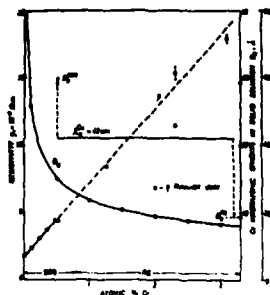
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The effect of rapid solidification (RS) of Cu-Cr alloys by melt-spinning and of subsequent aging on electrical properties are presented and discussed on the base of Matthiessen's rule, considering the rate of possible scattering mechanisms in total resistivity in the light of obtained results and literature data.

Electrical resistivity ( $\rho$ ) measurements on the 30-50  $\mu\text{m}$  ribbons of 2.3 and 3.1 at % Cr alloys indicate their complete supersaturation compared with maximum equilibrium solubility of 0.8 at. % Cr - the variation of the  $\rho$  with Cr concentration (see fig.) seems to be a simple extension of relation for solid-state quenching (SSQ) [1]. From measurements of SSQ alloys it is known that the sum of rates due to phonons and typical impurities can be evaluated as  $(1.80 \pm 0.05) \cdot 10^{-8} \Omega\text{m}$ . The rate of resistivity resulting from crystals defects retained from near the melting temperature does not exceed  $5 \cdot 10^{-11} \Omega\text{m}$ . The whole remaining rate of  $\rho$  comes from Cr atoms in solid solution and it makes about 90% of total resistivity for both Cu-2.3 and 3.1 at. % alloys. This can be interpreted as the result of much smaller spacing  $D_a$  between Cr atoms in solid solution in comparison with the mean free path of electrons in pure Cu ( $\lambda_e = 42\text{nm}$ , see fig.).

The  $\rho$  measurements on the ribbons aged at  $450^\circ\text{C}$  indicate that the observed considerable improvement of strength [2,3] occurs at the expense of conductivity which does not exceed 50% IACS for peak hardness and 60% IACS for overaged state in both alloys. The calculations based on the results of microscopic investigations [2] lead to the conclusion that this drop of conductivity is due to greater volume fraction of Cr particles and refinement of their dispersion. This makes for the marked decrease of interparticle spacing from about 60nm for SSQ to about 20nm for RS processing and the intensive scattering of electrons on the particles in the second case ( $D_{RS}^p < \lambda_e < D_{SSQ}^p$ , see fig.).

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EFFECT OF THERMALLY INDUCED STRUCTURAL CHANGES ON THE  
CORROSION BEHAVIOUR OF AMORPHOUS  $\text{Co}_{70,3}\text{Fe}_{4,7}\text{Si}_{15}\text{B}_{10}$  ALLOY

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The corrosion behaviour of amorphous alloys depends on their chemical composition, structure (degree of ordering, presence of crystalline nuclei and phase formations) and homogeneity of distribution of the chemical elements. From practical point of view it is important to determine the thermal stability of amorphous metallic alloys and changes in their physical and chemical properties as a consequence of lowtemperature heating. As known, upon that occur changes leading to enhance of the brittleness, lowering of magnetic anisotropy, enhance of coercive force.

The aim of this work is to investigate the effect of structural changes upon lowtemperature heat treatment of amorphous  $\text{Co}_{70,3}\text{Fe}_{4,7}\text{Si}_{15}\text{B}_{10}$  alloy on its corrosion behaviour. The alloy (produced by rapid quenching from the liquid state) is a perspective one for practical application as softmagnetic material with zero magnetostriction.

The specimens were vacuum heated at temperatures between 300 and 450°C, i.e. lower than the temperature of crystallization (500°C). The effect of structural changes on the corrosion behaviour of the alloy was studied by means of electrochemical technique, X-ray diffraction and electron microscopy, as well a computer program to determine the atomic short range order. Current-potential curves of the specimens in 1N  $\text{CCl}_3\text{COOH}$  were used for the determination of the corrosion parameters both for the active and passive state.

It has been found that the heat treatment, especially at higher temperature, yields to an increase of corrosion current and to a considerable decrease of susceptibility of the alloy to passivation. The decrease of corrosion resistance of the alloy has been related to the thermally induced structural change.

INTERACTION PAIR POTENTIALS FOR AMORPHOUS METALLIC ALLOYS

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The derivation of interatomic potentials for amorphous metallic alloys is discussed. This includes discussion of the possibility to derive the interatomic pair potentials from X-ray diffraction data on amorphous metallic alloys. A method applied originally to calculate the interatomic potential of mercury was used. After necessary accommodation, the interatomic pair potentials were calculated for amorphous metallic system containing two different types of atoms.

#### XIV.4

##### Selection and characterization of some amorphous ferromagnetic alloys

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dr.eng. Mihaiela Isac  
eng. Viorel Oltean  
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A comparative study is performed about equilibrium and amorphous structures for two alloys of composition prone to vitrification in the system Fe - B - C - Si and Fe - Ni - B - Si.

The selected compositions of the alloys are related to the commercial alloys Metglas 2605 and Metglas 2826 (or Vitrovac 4040). The choice of the composition was made among a large number of amorphous alloys on economical reasons (a minimum content of expensive alloying elements) and on a technical criterion (optimization of the properties specific to a soft ferromagnetic material). The equilibrium structures of the slowly cooled alloys and that of the amorphous ribbons made by melt spinning have been characterized by optical and electronic microscopy, microhardness and X ray diffraction.

ALL-ROUND SHAPE MEMORY EFFECT AND ITS  
PHYSICAL SIMULATION MODEL

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The preparation of all-round shape memory specimen is described in this paper. We try to explain the all-round shape memory behaviour by the help of a physical model proposed by Müller and suggest that the all-round shape memory effect is due to the fact that stress induced martensite of two different orientations is formed during the martensitic transformation in the outer and inner layers of the specimen respectively.

1



The thermomechanical behaviour and microstructure of Cu-Al-Ni  
single crystals with shape memory

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The shape memory effect has been observed in many alloy systems exhibiting a thermoelastic as well as a non-thermoelastic martensitic transformation. However, only a few systems remain attractive for the industrial application because of the price/quality ratio. The three important alloys are Ni-Ti, Cu-Zn-Al and Cu-Al-Ni.

An advantage of Cu-Al-Ni alloys is the higher  $M_s$ -temperature compared with both Ni-Ti and Cu-Zn-Al alloys, i.e., Cu-Al-Ni shape memory alloys can be used in higher temperature range. The polycrystalline Cu-Al-Ni alloys, however, cannot be cold worked and are generally brittle. Samples from these alloys would be broken along the grain boundaries on deformation of higher than 3%.

Since the Cu-Al-Ni single crystals show excellent reversible memory effect, the stepwise recovery on the thermoelastic martensitic transformation for the same alloy has been studied in our present investigation by means of complex load-deformation-temperature and microstructural behaviours. Recovery deformation of more than 8% has been observed in these single crystals.

Growth of CuZnAl and CuAlNi Single Crystals with Shape Memory Effects

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Shape memory describes the ability of certain metal alloys to be deformed at a temperature and then return to their original shape upon heating. This effect has been observed in several alloys. Presently, there are three groups of technologically applicable shape memory alloys, i.e., NiTi, CuZnAl and CuAlNi. A few investigators only, have studied the thermoelastic behaviour of the CuZnAl and CuAlNi single crystals having very low  $M_s$  temperature.

In our present investigation, a procedure is given for growing large single crystals of pure CuZnAl and CuAlNi by the Bridgeman method under high vacuum. Single crystals of the size of 75 mm length and 18 mm diameter have been produced and show  $M_s$  temperature are above room temperature. In order to characterize the material, it has been supplemented by x-ray microprobe and microstructural studies.

#### THE HYSTERESIS IN SHAPE MEMORY ALLOYS

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As is well-known the phase transition which produces shape memory is connected with a hysteresis. In this work we present measurements of pseudoclastic hystereses and hystereses in the deformation-temperature diagrams under different loads.

In some applications of shape memory alloys the hysteresis is welcome and one likes it to be wide. This is the case, if one uses shape memory alloys for clamps and splints, as in the medical field, or for couplings. In other applications the hysteresis is inconvenient, because it implies a dissipation. Thus in many of the proposed heat engines working with shape memory alloys the hysteresis loop traversed in each cycle signifies a loss.

Therefore the question arises as to how to control the size of the hysteresis. This report presents our attempts to influence the hysteresis loops by heat treatment and mechanical vibration.

## INTERFACE REACTIONS DURING MARTENSITIC TRANSFORMATION IN CU-ZN-AL SHAPE MEMORY ALLOYS

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Martensitic phase transformations are characterized by their hysteretic transformation behaviour. The origins of the transformation hysteresis are energy dissipative processes, whereby the frictional work to move the interfaces is thought to be an important contribution. During practical shape memory applications any effect influencing the transformation hysteresis can therefore promote the transformation in forward or reverse direction and cause that functional properties get irreversible. Until now the fundamental origin of those effects is not well understood.

The idea of the present study is to investigate the stability of the interfaces as well as their interactions during martensitic phase transformation in Cu-Zn-Al alloys, including those alloys, which are interesting for industrial applications. For that TEM in situ observations of martensite-austenite and martensite-martensite interface mobility have been carried out during thermal and stress cycling experiments. On the other hand internal friction measurements have been performed in an inversed torsion pendulum, measuring simultaneously the internal friction, the frequency, the electrical resistance and the shape change of the specimen.

TEM-observations show a high mobility of interfaces in these alloys indicated by a high sensitivity to small stress and temperature variations. The internal friction behaviour, which has been measured especially during partial temperature cycling and in dependence of oscillation amplitude, confirms that interface reactions as observed in the TEM can contribute to energy dissipative processes during transformation.

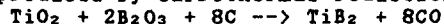
Titaniumdiboride (TiB<sub>2</sub>)

Formation of TiB<sub>2</sub>-layers of high quality on carbon substrate and TiB<sub>2</sub>(ZrB<sub>2</sub>)-production by cathodic deposition from fluoride melts

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Titaniumdiboride is an intermetallic compound of particular thermodynamic stability ( $\Delta H^0$  -246 kJ/mole) and mechanical strength. Usually it is produced by carbothermal reduction of TiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>.



and bigger parts are produced by sinter-pressing.

One of the potential applications of TiB<sub>2</sub> is for aluminium wettable cathodes for aluminium electrowinning processes (/1/ to /5/). For this application, however, sintered TiB<sub>2</sub>-parts seem to possess too little stability. Such parts are eroded at a rate which is from 20 to 100 times faster than would be calculated from the solubility of TiB<sub>2</sub> in liquid Al. The reason is the presence of TiO<sub>x</sub> and TiC in the intergranular phase which binds the TiB<sub>2</sub>-granules to each other. TiO<sub>x</sub> and TiC are preferentially dissolved so that the refractory metal erodes so fast. /6/

Cathodic TiB<sub>2</sub>-deposition

If TiB<sub>2</sub> is deposited cathodically on carbon support the generated TiB<sub>2</sub>-layers are almost dense at the C/TiB<sub>2</sub> interface, have a good adherence to the carbon support and are of almost stoichiometric composition and purity.

By voltametric investigation of cathodic Ti(Zr), B and TiB<sub>2</sub> (ZrB<sub>2</sub>) deposition from FLINAK-melts (FLINAK = Fluorides of Li, Na and K) one can clearly distinguish, that Ti(Zr) in absence of boron (dissolved in the melt in form of BF<sub>3</sub>) is deposited on carbon at much more cathodic potentials than B and that Ti together with B (Zr together with B) is deposited at a slightly more positive potential than boron alone. But this TiB<sub>2</sub> (ZrB<sub>2</sub>) deposition is observed only after reaching a certain cathodic overpotential - since on voltametric sweep reversal the voltage of zero current density which closely equals the equilibrium potential deviates from the potential of steep cathodic current rise for TiB<sub>2</sub>-formation by nearly 100 mV. This cathodic overpotential can tentatively traced back to initial boron-deposition.

Prolonged cathodic TiB<sub>2</sub> (ZrB<sub>2</sub>) deposition from FLINAK melts yields in formation of a TiB<sub>2</sub> (ZrB<sub>2</sub>) layer of very high purity and correspondingly very low erosion rates in liquid aluminium. The material can be deposited, too on more noble metals like copper. An expressed mismatch of thermal expansion of the metallic substrate and TiB<sub>2</sub> leads to only loose adherence of the refractory metal on the metallic substrate which allows to collect without difficulties the pure cathodically generated refractory metal. The adherence on carbon, however, is very strong and durable so that TiB<sub>2</sub>-coated cathodes can well be used in Al-smelters.

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XVI.2

Polycrystalline  $\text{CdSe}_x\text{Te}_{1-x}$  thin films prepared by  
electro-plating in aqueous medium.

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Cadmium chalcogenides as  $\text{CdTe}$ ,  $\text{CdSe}$  and the mixed compound  $\text{CdSe}_x\text{Te}_{1-x}$  are interesting materials which can be used as polycrystalline thin films in photovoltaic or photoelectrochemical devices for the conversion of the solar energy.

$\text{Cd}$ ,  $\text{Se}$  and  $\text{Te}$  were successfully codeposited by cathodic electrodeposition which is a cheap and easy-to-manage method. However the layers had to be heat-treated to crystallize and to get semi-conducting properties. The aim of this work is to investigate the electrochemical process which leads directly to a crystallized  $\text{CdSe}_x\text{Te}_{1-x}$  compound. The deposits are made potentiostatically from a sulphate solution containing  $\text{TeO}_2$  and  $\text{H}_2\text{SeO}_3$  in various amounts. The composition, the crystal structure, the morphology, the band gap width and the photo response of the electroplated layers are studied as functions of the composition of the solution and of the electrochemical parameters.

It is shown that the crystallized compound is obtained in a narrow potential range corresponding to the under-potential deposition of cadmium and to a plateau current limited only partially by the convective diffusion of chalcogenide ions.

### XVI.3

#### Influence of the interfacial adsorption on the texture and the microhardness of nickel electrodeposits.

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In the nickel electrocrystallization process appears a strong specific inhibition of crystal growth. The different chemical species, such as  $\text{Ni(OH)}_2$ , gaseous  $\text{H}_2$  or  $\text{H}_{\text{ads}}$  which exist or formed in the metal-electrolyte interface according to the conditions of the electrolysis, are selectively adsorbed in the continually regenerated metallic surface and impose on the texture of the electrodeposits.

The purpose of this work is to study the correlation between the texture and the microhardness of nickel deposits. The preferred orientation of the electrodeposits, prepared from all sulfate and all chlorate baths, is studied by X-ray diffraction and the corresponding diagrams of textures are traced, as a function of both the solutions pH and the cathodic current density. The microhardness of deposits is determined by the Vicker's method.

It is shown that the textures and the microhardness of the deposits depend on the conditions of the electrolysis, but the hardness seems to be independent of the crystallites orientation, in spite of the related bibliographic references. The preferred orientations and the microhardness of the nickel deposits are produced by the same cause: the specific inhibition of the cathodic surface during the electrodeposition imposes on the orientation of the crystallites, provokes the deformation of the crystal lattice and increases the hardness of the deposits.

XVI.4

The autocatalytic build-up process and their special interfaces.

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The formation of electroless Ni-P films on different metallic surfaces is examined. Aspects of the nucleation process, and of the structural and electronic properties of the deposited layers as well as the stabilisation of amorphous structure is studied by depth-dependence of deposited films.

We investigate the solid-aqueous solution interface and the special complexes participated in the formation.

These experiments indicate special sequences in growth, depending on the substrate. We discuss the growth steps, in terms of chemical bonding of the phosphorous within the layers.



"Modification of microstructure and properties in nickel electrodeposits by using reversed current"

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The most common technique followed for the electrodeposition of metals usually involves the application of direct current. By the end of 1970 however, a technique for the electrodeposition of metals was introduced involving the use of reversed or pulse current.

This technique perturbs the electrocrystallization process and as a result changes the structure and the properties of the deposits. The effect of the reversed current in the electrocrystallization mechanism depends on two new parameters: the pulse frequency  $\nu$  and the duty cycle  $T_1/T_1+T_2$ , where  $T_1$  is the deposition time (cathodic period) and  $T_2$  the dissolution time (anodic period).

The purpose of this work was to study systematically the changes of the orientation and the properties occurring on nickel deposits, prepared from Watts electrolytic bath, with the application of reversed current. The preferred orientation is identified by X-ray diffraction, the microstructure is studied by SEM and TEM techniques and the microhardness and the roughness of the deposits are also examined.

It was observed that variations of the characteristic parameters of the reversed current result in total modification of the texture, the microstructure, the surface morphology and the properties of the deposited metal.

Keywords: nickel electrocrystallization, reversed current, texture, microhardness, surface morphology, roughness.

The Optimal Technology of the  
Preparation of TiNi Fixation  
Elements

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The aim of the presented paper is to give an optimal technology, as related to the manufacture and performance of some fixation elements on the basis of TiNi. Materials with different thermo-mechanical treatments were investigated for their deformation behaviour and structural characteristics. The materials were rolled at various temperature levels from 25 to 800°C and then subjected to annealing at temperatures in the range from 200 to 400°C for one hour. If the rolling temperatures are lower than 750°C, subsequent heat treatment further modifies the dislocation density. The stresses necessary to induce the B2 → B19' phase transformation, or reorientation of B19' martensite variants, are approximately twice as great in hardened materials, as in materials annealed for one hour at 400°C. Matrix strain hardening affects the stability extent of the basal structural components. An increase of the dislocation density leads to a decline of the  $M_s$  point and supports the occurrence of rhombohedral R phase. The optimal technology, as regards suitable mechanical interactions of the fixation elements with living tissues, is based on hot rolling at 500°C. This treatment produces a structure with a convenient dislocation density and this structure can be further modified by subsequent annealing to reach appropriate recovery stresses of fixation elements.

## FAILURES OF ORTHOPAEDIC FIXATION DEVICES

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YUGOSLAVIA

Since the first use of chromium nickel molybdenum steels for implants in the thirties, rapid progress has been made in the development of stainless steels. In agreement with the characteristic potentials for localized corrosion, a statistical evaluation of failures shows that pitting, crevice corrosion and corrosion fatigue as a result from the later can easily be avoided by higher contents of chromium and molybdenum. A number of cases where material defects have resulted in fracture have also been reported. Stress corrosion cracking of the alloys commonly used and under the conditions present *in vivo* is a rare occurrence. A vast percentage of the surgical implants fabricated are made from 316 L stainless steel, the cast Co-Cr-Mo-C alloy and Ti - 6 Al - 4 V. Here additional examples of implants which have failed *in vivo* during service life are presented, specially hip prosthesis failures. The investigated prosthetic hip joints were produced from 316 L stainless steel in wrought form and from cobalt chromium base alloy in cast form, where the related factors, contributing to the failure, are discussed. Two different modes of fracture were obtained as a result of fractographic analysis of the broken implants. The fracture of the prosthetic hip joint produced from 316 L stainless steel resulted from the propagation of two cracks initiated on parallel planes being slightly displaced relative to each other and perpendicular to the stem axis. Propagation and joining of the two cracks resulted in a step on the fracture surface. A number of fatigue cracks was observed on the inner surface of the stem. The fractures of the stems produced from cast cobalt chromium base alloy showed typical plain fracture, with no surface cracks on the stem. The results of metallographic structure determinations showed that here again the fracture mode of the stem was fatigue fracture mode, but typical for cast alloy.

**BIOCOMPATIBLE FIBRE COMPOUNDS: AUTOMATED ANALYSIS OF QUALITY PARAMETERS BY COMPREHENSIVE IMAGE PROCESSING.**

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Failure of load transmitting surgical implants, i. e. shafts of total hip endoprostheses, followed by reoperation, or success described by lifelong biocompatibility between implant and human tissue, besides accurate designing, mathematical modelling and calculation, highly depend on three main specifications when a fibre compound is used as biomaterial: fibre content, fibre distribution and quality of the fibre/matrix interface. A new method has been developed in order to automatically determine the fibre content and a specific homogeneity factor for thin lamiantes as well as for thick fibre reinforced composites by modification of a professional image analysis system (Tracor Northern 8502) to an automatic scanning tool of microscopic ground sections of a specimen; angles of fibers within the specimen are also detected and displayed in a histogramme. The result is an immediately available data sheet characterising the quality of the processed material. It is easy to apply, ready for multiple applications in short time and thus a powerful control instrument of manufacturing process dependent parameters. It is designed to replace time consuming, hazardous and irreproducible chemical methods of determination of fibre contents. Worked out for biomaterials of orthopedic implants it can also be applied for reproducible characterization of other anisotropic materials.

The method of application to thermoplastic and duroplastic carbon- and glassfibre compounds, detailed output data, statistical analysis of reliability and experimental comparison with current chemical methods are presented.

**Key words:** biomaterial, anisotropic material, fibre content, fibre/matrix ratio, fibre/matrix homogeneity, quality standard.

#### XVII.4

##### MECHANICAL PROPERTIES VS MICROSTRUCTURAL FEATURES RELATIONSHIP IN COW FEMUR

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The work reported here was a part of an investigation of the relationship between microstructural aspects and mechanical properties of structural bones. Wet cow femurs with and without notches were used in the mechanical tests. While whole cow femurs were broken in the three-point bend tests the compression samples were prepared with various  $L$  (length)/ $D$  (diameter) ratios. From the load vs. displacement curves the bending strength, elastic modulus and specific displacement were obtained as 50-150 MPa, 1-5 GPa and 2-4%, respectively. The compressive strength and maximum compressive strain also varied between 40-100MPa and 1-4%, respectively. It was noted that the bending strength was reduced only when the notch made on the femur surface exceeded one-third of its thickness. An increase in the cross-head speed increased the bending strength and specific displacements whether the femur was notched or not.

The details or microstructural features were examined using optical microscope, scanning electron microscope and also x-ray powder diffraction. Both the microstructure and also the fracture surface of cow femur were found to resemble the human femur rather closely. X-ray powder diffraction data revealed that the hydroxylapatite phase in the cow femur was mostly in an amorphous form. Vicker's pyramidal hardness values measured on the metallographic samples varied between about 40 VPN near the surface and 60 VPN away from the surface.

IMPROVING BLOOD COMPATIBILITY OF POLYETHYLENE  
TEREPHTHALATE BY ION BEAM TREATMENTS

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In /1/ it was established a surface energetic criterion of blood compatibility of foreign surfaces: the blood-biomaterial interfacial tension  $\gamma_{SL}$  must be of the order of 1-3 mNm<sup>-1</sup> (the magnitude of the cell-medium interfacial tension) in order to comply with the dual requirements of a low driving force for the adsorption of blood components and a mechanically stable blood-biomaterial interface.

Polyethylene terephthalate (PET) possess some desirable qualities for blood contact applications (like good mechanical strength, chemical inertness to blood components, nontoxicity etc), but it is a nonpolar material ( $\gamma_S^P = 0,67 \text{ mNm}^{-1}$ ), which results in his high interfacial tension with blood plasma, ( $\gamma_{SL} = 50,8 \text{ mNm}^{-1}$ ).

In order to improve the blood compatibility of such material, it is necessary a considerable increase of his polar surface free energy component. In the paper we present some results concerning the modification of the surface free energy components of the PET by treatment with ion beams, obtained with a multipolar ion source. We investigated the influence of the working gas, ion energy and exposure time on the  $\gamma_S^P$ ,  $\gamma_S^d$  and  $\gamma_{SL}$  values.

As for the discharge treatments of PET /2/, the reactive gas (oxygen) seems to be more adequate than the inert one (argon) for the modification of the surface energy.

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**A TECHNIQUE FOR BRAZING ALUMINIUM NITRIDE SUBSTRATES.**  
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A technique for brazing aluminium nitride (ALN) using conventional (non-active) brazing alloys has been investigated. The process involves the in-situ decomposition of a metal hydride. This process alters the surface chemistry of the substrate and improves the wettability of the molten braze. The development of high strength bonding between braze and ceramic results. The ceramic-braze interface was studied using scanning electron microscopy (SEM). The nature of the interfacial reactions and the reaction products have been identified using x-ray diffraction (XRD). The progress of the reaction has been followed using differential thermal analysis (DTA).

The experimental results have been correlated with thermodynamic predictions of the reaction process. In addition to joining ceramic to ceramic, braze joints of ALN to copper and to a low expansion iron-nickel lead frame alloy were made.

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INTERFACIAL REACTIONS IN  $\text{Al}_2\text{O}_3$ -TO-TA6V  
AND  $\text{ZrO}_2$ -TO-TA6V BRAZEMENTS

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Chemical reactions occurring during brazing between TA6V titanium alloy and ceramics such as  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  were investigated. A high reactivity of a Cu-40Ag-5Ti active braze alloy with these materials was observed, leading to the formation of interfacial reaction products which were characterized by electron microprobe analysis and transmission electron microscopy.

At the braze/ceramic interface, a continuous layer of  $\text{Cu}_2\text{Ti}_4\text{O}$  was formed. Starting from the base metal, a sequence of Cu-Ti intermetallic phases was observed.

Results are discussed in relationship with the mechanical behaviour of the joints. They show that the tensile strength of the  $\text{ZrO}_2$ /TA6V joints is much higher than that of the  $\text{Al}_2\text{O}_3$ /TA6V joints.



**INFLUENCE OF DOPING ELEMENTS AND GEOMETRY ON THE INTERFACE REACTIONS  
BETWEEN SiC AND Ti.**

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In the last years SiC reinforced titanium matrix composites have been developed for aerospace applications. Their mechanical properties depend on the chemical reactions occurring at the interface. The chemical composition and the thickness of reaction scales which form at the interface depend on the metal and ceramic composition and on the geometry at the interface. Therefore, we have studied AVCO SCS6 fiber / Ti-6Al-4V composites and one dimensional diffusion couples SiC / Ti and SiC / TA6V. We have determined the microstructure and the chemical composition by transmission electron microscopy, electron probe analyses and by secondary ion mass spectrometry.

In linear diffusion couples SiC/Ti,  $Ti_{1-x}$  and  $Ti_2Si_3$  were identified as reaction products at 1200°C. Near the SiC-interface both phases are found in form of small grains in about equal quantities. Within the product scale the stoichiometry of titanium carbide and titanium silicide vary from carbon rich compounds near SiC to less carbon rich compositions on the metal side. The reaction kinetics have been determined.

In composites fabricated at 925°C the results are slightly different. The reaction scale consists of three layers spreading from the fiber to the metal matrix : (i) small titanium carbide grains (diameter 20 nm), (ii) larger titanium carbide grains (diameter 100 nm) and (iii) large titanium silicide grains (diameter 100 nm). Aluminum and vanadium profiles have been measured within the reaction zone.

The reaction products for composites and one-dimensional diffusion couples will be compared and the mechanism for first contact between metal and SiC and longer reaction times will be discussed.

## INTERFACE REACTION BETWEEN TITANIUM AND SILICON NITRIDE

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The products of the interface reaction between Ti-deposited film and the pressless sintered  $\text{Si}_3\text{N}_4$  substrate in the range of 833K-1273K vacuum were studied by x-ray diffraction analysis. When the reaction temperature does not exceed 973K, no reaction product between Ti film and  $\text{Si}_3\text{N}_4$  substrate is observed, only crystallization of the Ti film itself takes place in this stage. When the reaction temperature is in the range of 1073K-1123K, the reaction products  $\text{Ti}_2\text{N}$  and  $\text{Ti}_5\text{Si}_3$  are observed. When the reaction temperature is at 1173K, the reaction product  $\text{Ti}_2\text{N}$  transforms to TiN. Finally when the reaction temperature is as high as 1273K, the reaction products TiN and  $\text{Ti}_5\text{Si}_4$  are observed, while the Ti metal film diminishes completely. The fact that the lattice parameter of  $\text{Si}_3\text{N}_4$  is unchanged throughout postannealing show Ti atoms not being dissolved into  $\text{Si}_3\text{N}_4$  lattice.

Interaction between  $\text{Si}_3\text{N}_4$  and transition metals.

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The interfacial reaction between  $\text{Si}_3\text{N}_4$  and transition metals (Ti, Cr, Fe, Ni) at the temperature range 700-1100°C has been studied in order to investigate the reaction in the initial stage of the process. The reaction products are analyzed by X-ray diffraction and for microstructural analysis, by optical microscopy, scanning electron microscopy and electron probe micro analyzer. The products of the reaction detected both in metal and in  $\text{Si}_3\text{N}_4$  are nitride and silicide in the case of Ti and Cr, but no reaction products have been found in the case of Fe and Ni at temperatures below 1100°C. Compared to SiC,  $\text{Si}_3\text{N}_4$  reacts to a much lesser extent, presumably because of the influence of oxygen in the atmosphere on the  $\text{Si}_3\text{N}_4$ -metal reaction and the thermal decomposition of nitride.

Thermodynamic considerations of the Me-Si-N ternary diagrams applied to the tie-lines support the experimental results. When phase diagrams show possible formation of many silicides, the formation of the thermodynamically most stable silicide is in reality formed.

**Study of the phase transformation occurring during the  
interfacial reduction of Hematite.**

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During the interfacial reduction of iron oxide, there is a phase transformation : the rhombohedral lattice of  $\text{Fe}_2\text{O}_3$  is transformed into the cubic lattice of the magnetite  $\text{Fe}_3\text{O}_4$ . One can observe by scanning electron microscopy on reduced single crystal that the interface of the reaction remains parallel to the outside surface.

The crystallographic orientation of the magnetite is studied according to its location between the interface and the outside surface by texture goniometry. Several kinds of orientation are observed.

One can say that :

1) at the very beginning of the reaction, when the surface is close to the outside surface, there is a topotactical relationship between hematite and magnetite,

2) then because the stress field in the magnetite layer new orientations appear at the "interphase",

3) simultaneously, in the new phase, all the orientations observed tend to other orientations because the sintering effect.

The orientation of the new phase with respect to the previous one depends on the behaviour of the reaction.

**USE OF SILANES AS ADHESION PROMOTORS FOR STEEL IN THE  
PRESENCE OF CATHODIC PROTECTION.**

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Corrosion protection of steel structures under water, is usually based on either cathodic protection, protection by an organic coating or a combination of both. When an organic coating is used, the weak point is the adhesion between the coating and the steel substrate. In laboratory tests this is clearly demonstrated by the steady decrease in the measured adhesion as a function of time of exposure to the wet environment. It is known that some organo-silanes can act as adhesion promoters at the interface between the steel and coating material, and thereby greatly increase the retention of the wet adhesion.

In this work we have studied the effect of amino- and diamino-silanes at the interface between mild steel and a fusion bonded epoxy coating. The experiments reported have been designed to study of the effect of the chemical interactions at the interface. They lead to a better understanding of the chemical reactions involved in the generation of this improved adhesion. The effect of silanes on the wet adhesion is studied for the cases where the steel is cathodically polarised and where it is unprotected. Under cathodic polarisation, the pH under a coating can rise to as high as 13.

With the aid of XPS and reflectance FT-IR (ATR and RAS) the resistance of the steel silane bonding has been studied as a function of both temperature and pH. Results indicate that the silane metal bonding is stable under neutral conditions (pH 7) even at elevated temperatures. At high pH, however, the silanes are observed to be susceptible to hydrolysis even at relatively low temperatures. The above results are correlated to adhesion measurements and cathodic disbondment tests made on epoxy steel coating systems.

**INVESTIGATION OF PHASE TRANSFORMATIONS IN IRON OXIDE LAYERS  
BETWEEN STEEL SUBSTRATE AND POLYMER COATING**

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The phase transformations in oxide layers below an organic coating have been investigated in-situ by transmission Mößbauer spectroscopy.

If an oxide covered iron surface is coated with an organic polymer, the reduction of the Fe(III)-oxides below the coating allows a further corrosion without any diffusion of  $O_2$  through the polymer. Immediately after wetting the polymer coated surface  $H_2O$ , will diffuse through the polymer layer and the oxide is polarized cathodically by the underlying iron surface. First, the  $\gamma$ -FeOOH crystals are partly reduced in the given crystal structure. This reaction is accompanied by the diffusion of  $H^+$  into the lattice of  $\gamma$ -FeOOH. The anodic reaction is the dissolution of iron. As a second reaction the transformation of  $\gamma$ -FeOOH into the cubic lattice of  $Fe_3O_4$  due to diffusion of  $Fe^{2+}$  into the lattice of  $\gamma$ -FeOOH is observed. Below organic coating, where the  $Fe^{2+}$ -concentration is rather high, large amounts of  $Fe_3O_4$  are found. The formation of  $Fe_3O_4$  changes the oxide morphology and causes a loss of adhesion of the polymer film as could be confirmed by adhesion measurements.

The above described phase transformations are strongly dependent on the electrolyte conductivity below the organic coating, e.g. on the content of soluble  $SO_4^{2-}$ , which results from the adsorption of  $SO_2$  from the atmosphere. In the absence of any soluble  $SO_4^{2-}$  the reactions are inhibited to a great extent.

As the redox-reactions inside oxide layers are of ultimate importance for the adhesion of the polymer film, possible means are described to retard such reactions by modification of the oxide surface or the oxide composition.

**Chemical Compatibility of Coated Systems at High Temperature**

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With increasing gas inlet temperatures in gas turbines and increased blade temperatures interdiffusion effects between coatings and superalloys becomes very important. Interdiffusion may result in a change of the coating composition or substrate composition and severe degradation of the coating. These effects are strongly dependent on the coating composition. Typical effects described in this paper are dissolution of Al-rich phases in the coating and formation of mixed aluminides and other intermetallic phases in the interdiffusion zone, dissolution of carbides and borides from the alloy and subsequent precipitation of these phases in the coating or interdiffusion zone and the formation of Kirkendall porosity due to high diffusional fluxes. For many systems these effects can be semiquantitatively estimated by thermodynamic calculations.

Examples will be given, to improve thermodynamic activities of important alloying elements in the coating or alloy. To avoid chemical incompatibility, it is important to accommodate the chemical composition of the coating and the bulk alloy for further alloy development.

Interfacial reactions in metal matrix/metallic glass  
composites

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Good adhesion between matrix and reinforcing fiber is one of the crucial factors which determine the mechanical behaviour of a composite material. Annealing of metal matrix composites is known to improve adhesion by diffusional bonding, but metallic glasses usually exhibit severe embrittlement during such a heat treatment.

In primary crystallizing glasses, however, embrittlement is reduced during primary crystallization, ductility and strength is regained in the partially crystallized state. Interfacial reactions during annealing has been studied systematically by cross-sectional TEM in composites of  $\text{Fe}_{42}\text{Ni}_{42}\text{B}_{16}$  metallic glasses embedded in a crystalline nickel matrix. It has been observed that during primary crystallization in the bulk of the ribbon very fine  $\gamma$ -(Fe,Ni) crystals grow from the nickel matrix into the original glass thus producing a new interface with excellent adhesion.

Another way to produce metal matrix/metallic glass composites with extraordinary interfaces has been found in the formation of glasses by solid state reactions. A skilful heat treatment of a heavily compacted suitable mixture of nickel and zirconium powder will lead to the formation of amorphous layers within a nickel matrix by solid state diffusion.



## TEM Examination of Cu-Fe and Ni-Fe Metal Multilayers

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Our work in the past on the use of TEM for the characterization of metal multilayers made by sputter deposition has concentrated on the determination of the accuracy to which the local in-situ strains can be measured for coherent (100) layers of fcc systems (notably Cu-Ni/Pd) as a function of the layer wavelength. This enabled us to demonstrate that, for example, the moduli are definitely affected quite grossly (and presumably as a function of Brillouin Zone interaction effects) below the critical wavelengths at which the properties can perhaps become anomalous.<sup>(1)</sup>

Metal multilayer systems are also interesting however for the examination of phase transformations and this area of study is less controversial than those related to the reasons for wavelength dependent property changes. Here we report our first preliminary results on the Ni-Fe and Cu-Fe systems as layered on (100) planes. The main emphasis of this first stage of our work on these systems has been on determining the critical layer thicknesses above which a) pseudomorphic (metastable fcc) Fe layers first lose their coherency with the formation of interface misfit dislocations and b) the fcc Fe transforms to the bcc structure. The interesting point is of course that these changes do not necessarily occur at the same wavelengths. We will report our data in this context for layer wavelengths of between 1 and 5 nm and discuss too the related transformation behaviour of particulate Cu in Fe.

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Contact-reactions at thin film Aluminum - Transition metal  
Interfaces

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Interfacial reactions at thin film Al/Cr and Al/Zr interfaces have been studied by means of cross-sectional transmission electron microscopy.

Whereas rather smooth, planar growth of  $\text{Al}_7\text{Cr}$  occurs in the case of Al/Cr, an irregular growth of  $\text{Al}_3\text{Zr}$ -spikes along Al-grain boundaries has been observed in the case of Al/Zr. For comparison the decomposition behaviour of rapidly solidified Al(Cr) and Al(Zr) supersaturated solid solutions upon thermal annealing has been studied.

Based on the observed morphologies and orientation relationships a model will be proposed for the different modes of interfacial reactions, i.e. planar or irregular growth.

Interface reactions during ion beam assisted  
deposition of Al films

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Aluminum films of  $\approx 5 \mu\text{m}$  thickness were deposited on oxidized Si-wafers at  $T \approx 250^\circ\text{C}$  by UHV evaporation techniques. The change of the microstructure due to ion bombardment during evaporation was investigated by X-ray techniques. A systematic variation of the amount of gas incorporation was achieved by varying the energy  $E$  of the Xenon ions ( $0.1 \leq E \leq 1.5 \text{ keV}$ ) and the normalized energy  $E_N$  ( $0 \leq E_N \leq 200 \text{ eV/Al atom}$ ). The results will be discussed in terms of the change of texture, stress, and grain size as a function of the normalized energy and/or the gas content: i) For  $E_N \approx 0$  the well-known  $\langle 111 \rangle$  fibre structure is observed. The observed film stress of  $\approx 35 \text{ MPa}$  can be understood by the thermal stresses due to the cooling of the films and their relaxation to a value close to the yield stress. ii) For  $5 \text{ eV} \leq E_N \leq 80 \text{ eV}$  a characteristic tilt of the fibre axes by  $\approx 20^\circ$  is observed. This tilt is explained by an ion beam assisted interface reaction of the Al with the oxygen of the  $\text{SiO}_2$  substrate. This model is supported by the fact that the tilt is not observed for Ti/TiN interfaces and after deposition at a buffer layer of Al (with  $E_N = 0$ ). In addition the variation of the film stress will be discussed. iii) For the highest values of  $E_N$  ( $\approx 100\text{--}200 \text{ eV}$ ) a  $(111)$ - "single crystal" texture is observed that is determined by the ion beam direction.

Interfacial Reactions during Mechanical Alloying

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Mechanical alloying is a non-equilibrium processing tool which can be used to form metastable alloys, like amorphous metals or quasicrystals. Starting from the elemental, crystalline powders, ball milling first produces powder particles with a characteristically layered microstructure. Further milling refines this microstructure more and more and leads to an ultrafine composite with an elemental layer thickness in the range of 10 to 20 nm. An atomic mixing of the elements only by deformation is not possible. The formation of the new phases starts as a reaction at the interfaces between the different elements. Further growth requires an interdiffusion through the newly formed phase which can occur because of the considerable temperature rise in the powder particles during the collisions of the balls in the mill. These results show that the formation of metastable phases by mechanical alloying is closely related to solid-state reactions in layered composites prepared by evaporation or mechanical codeformation.

SOLID STATE REACTIONS IN THE Ni-Sn SYSTEM INDUCED BY  
COLD-ROLLING AND MECHANICAL ALLOYING

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Extensive cold-rolling of thin sheets and mechanical alloying of powders has been performed at room temperature in order to examine the Solid State Reactions (SSR) between Ni and Sn at the average compositions Ni<sub>75</sub>Sn<sub>25</sub> and Ni<sub>60</sub>Sn<sub>40</sub> (at. %). As shown by X-ray diffraction, in all cases the first step of the SSR is the formation of Ni<sub>3</sub>Sn<sub>2</sub>. On the basis of the diffusion coefficients, the formation of Ni<sub>3</sub>Sn<sub>2</sub> is interpreted as the result of Ni diffusing into Sn rather than viceversa. The reaction rate is approximately linear with the number of deformation cycles up to the point where all Sn is consumed. Further processing at both compositions induces the formation of Ni<sub>3</sub>Sn and Ni<sub>3</sub>Sn<sub>4</sub>. This step, according to the relative X-ray intensities, does not seem to be the result of simple decomposition of Ni<sub>3</sub>Sn<sub>2</sub>. No appreciable broadening or shifting of the diffraction peaks is observed up to this point, thus implying the the entire system after the deformation relaxes to a near stable equilibrium state.

In the case of cold-rolled samples further deformation introduces considerable changes in the diffraction peaks of all phases. A decrease of their integrated intensities is accompanied by significant broadening and, in the case of Ni, by an angular shift. In addition one observes a notable increase of the background intensity which could be attributed to diffuse scattering from a disordered (amorphous-like) phase. No such transformations are observed in the mechanically alloyed samples. Electron probe chemical analysis shows that the oxigen contamination in the extensively cold rolled samples is considerably higher than in the ball milled ones, thus suggesting a possible explanation for their different behaviour.

HIGH-TEMPERATURE BRAZING OF NICKEL ALLOYS.

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Nickel-based alloys for high-temperature service, such as gamma prime or oxide dispersion hardened alloys, are generally non weldable and alternative joining processes are therefore required. In addition many elevated-temperature applications, especially in the aerospace field, are incompatible with fusion welding because fabrication of thin walled structures or the joining of nickel alloys to dissimilar materials is required. A possible solution to these fabrication problems is provided by high-temperature vacuum brazing at temperatures in excess of 900 C using nickel-based filler metals containing melting-point depressants such as boron, silicon and phosphorus. The use of suitable post-braze heat-treatments can result in the dispersion of the melting point depressant in the substrate so that parent-metal mechanical and service temperature properties can be attained by brazed components.

The wider application of nickel-based high-temperature brazes is, however, limited by the difficulty of obtaining stable wetting. Most previous studies have examined this problem by in terms of the wetting behaviour of specific combinations of filler and base metals. The main aim of the work described in this paper is to produce a general model for the mechanisms of wetting and flow in high-temperature brazing which accounts for the effects of compositional and process variables.

Experimentally, the effects of substrate and filler composition and process variables (vacuum quality, temperature and time at temperature) on wetting and flow have been assessed using the sessile drop technique. In addition, microstructural investigations, including electron and hot-stage microscopy, micro-analysis and X-ray diffraction, have been conducted. The results have confirmed general hypotheses for the mechanisms controlling braze spreading:

- 1: overall spreading is controlled by braze metal chromium content;
- 2: spreading of phosphorus-bearing brazes without chromium is controlled by the substrate oxide;
- 3: in boron-containing fillers, the boron reduces the substrate oxide in a reaction which exerts a fluxing effect. Subsequent spreading is controlled by alloying reactions between the braze and substrate.

TITLE: REAL TIME OBSERVATIONS OF THE WETTING AND SPREADING BEHAVIOUR  
OF NICKEL BRAZE ALLOYSAUTHORS: J.C. Ambrose and M.G. Nicholas  
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The high temperature vacuum braze alloys based on nickel or nickel-chromium with additions of melting point depressants, phosphorus or boron and/or silicon, are used in the aerospace and nuclear industries for joining critical components made from steels and nickel alloys. Successful brazing depends on the filler metal being able to wet the component pieces it is to join, but there is little information in the literature on the wetting behaviour of the nickel filler metals.

This paper describes some of the work done to investigate the effects of braze alloy and workpiece chemistry on the wetting and spreading behaviour of several nickel braze alloys. Initially, simple area of spread tests were carried out in which controlled amounts of the nickel braze alloys were melted on pieces of a wide range of commercially available alloys, including austenitic and martensitic steels and some nickel alloys. These tests showed that the area to which brazes spread in a given time varies with the chromium content of the workpiece alloy. For the Ni-11%P eutectic filler metal, it was found that, in general, increasing the chromium content of the workpiece restricted braze spreading. Similar behaviour was observed on laboratory produced iron-chromium binary and iron-chromium-nickel ternary alloys.

The behaviour of the Ni-11%P braze has been studied in detail, using in particular, a heating stage fitted on a light microscope which enables the braze alloy to be observed as it melts and spreads out on the workpiece. The melting sequences are recorded in real time on video tape. This technique has shown that the Ni-11%P braze alloy resolidifies at its melting temperature once it has melted and spread out on both Fe-2%Cr, and Fe-20%Cr but the braze resolidifies more quickly on Fe-20%Cr than on Fe-2%Cr. It is thought that this behaviour is due to dissolution of the workpiece material and consequential dilution and complexing of phosphorus to increase the braze melting point and viscosity.

The heating stage fitted on the light microscope has also been used to observe spreading of the braze alloy beneath the oxide on the workpiece. The kinetics of braze flow have been studied and observations made of the effects of the workpiece surface topography on the rate of braze flow.

## NEW COATING CHARACTERIZATION TOOLS

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In the field of protective and wear-resistant coatings, the scratch- and ultramicrohardness testers are becoming necessary and well established tools to control and characterize mechanical properties of surfaces, interfaces and phase boundaries.

The Ultramicrohardness tester (UMD), presented here, is based on the penetration depth measurement during a loading and unloading cycle with specially shaped indentors : three or four symmetrical faces . This "depth sensing" provides a means for evaluating elastic and plastic deformations of the indented material. This leads to the determination of hardness values, provided the geometrical quality of the indenter is well known.

The Critical Load,  $L_c$ , determined by the scratch test is widely regarded as being representative of coating adhesion behaviour. It remains difficult to express the adherence quantitatively because the Critical Load depends on several parameters related to the testing conditions and to the coating/substrate system.

An other part of this poster is related to the instrument, REVETEST<sup>®</sup>, to control the adhesion of the coatings to the substrate, through scratching the surface with a wear-resistant indenter. The scratch test method is basically a comparison test. Therefore, it is useful to create a library, which collects the data obtained by this characterization method. This enables the user to compare Critical Load data obtained on a wide variety of coating/substrate combinations. To develop such a data base, the necessary software has been developed.

Each record corresponds to a measurement; some fields are used to characterize the sample, others to memorize the scratch test results. The data base can be questioned or searched for different parameters such as substrate, coating thickness, hardness etc.

To provide increased efficiency in the use of the CSEM REVETEST, Automatic Scratch tester, additional control and manipulation possibilities are offering :

- Full control of scratching operation,
- Comprehensive measurement data acquisition with D/A input & output,
- Program based on menu approach with monitor, printer or plotter output

First, the software program will check and display : the position of the table, the START, STOP & RESET switch positions, the min and max force settings  $F_{min}$  &  $F_{max}$  respectively, the table speed and loading rate settings,  $V_y$  &  $V_x$ , the loading range switch position  $i = 200$  N or  $100$  N. The required instrument configuration is set on the electronic control unit or through the keyboard. The user then can start the measurement run which will proceed automatically.

Next, the data acquisition procedure will store, for each run, the acoustic emission signal and friction force with their corresponding normal load and scratching distance values. Their real-time graphic representation on screen will be implemented, together with printer and plotter output files.



CHARACTERISATION OF ADHESION BY THE  
OESM METHOD AND MEEM

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The optical emission under mechanical stress (OEMS) method was previously introduced as an alternative method in the study of materials, especially adhesives, under high mechanical stresses. In this paper we report on further developments of this method, as used in the characterisation of metal/polymer interfaces, and we introduce the mechanical excited emission microscopy, MEEM.

The OEMS method consists in monitoring by electronic or photographic means the optical emission occurring at the interface at fracture. The method allows the visualisation of fracture patterns and the determination of fracture micromechanics. In this paper we introduce the following quantitative parameters to describe the adhesion quality: number of fracture lines per unit length; number of fracture points, as evidenced by optical emission, per unit area; the mean area of fracture points; the stress threshold for optical emission; the mean angle of the fracture lines with respect to the stress direction; number, mean diameter and shape of the detaching regions, and the mean gradient of the light emission at constant stress, and its variance.

Moreover, we introduce the MEEM technique, allowing the direct visualisation of microfracture phenomena. The device used consists in a classical microscope and an independent testing table adapted to resist at mechanical shocks without significant deformation, with the appropriate stress applicator, the stressing chamber being optically isolated from the ambient.

**Investigation Of The Corrosion Reaction Under Organic Coatings  
With AC-Impedance Spectroscopy**

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The problem for electrochemical measurements at coated metals is the high resistance of the coating, which impedes the measurement of the polarisation of the metal surface due to a ac- or dc-current. In order to solve this problem a second reference electrode is placed beneath the organic coating, but isolated from the sample. The system under test is an iron sample, coated with an alkyd resin in 0.1 N NaCl. This second reference electrode is used to measure the potential drop at the metal/polymer interface as well in dc-polarisation as in ac-impedance type measurements. This impedance measurements using an additional, second reference electrode are totally new and give informations about the corrosion reaction beneath the organic coating at the phase boundary metal/organic coating and about the structure of the interface.

The impedance measurements shows:

- The mechanism of the corrosion reaction under the coating is similar to that of an uncovered metal in the same solution.
- The capacity of the double layer (of the free surface) is much smaller than the capacity of uncovered iron in the same solution. Therefore the ions and H<sub>2</sub>O are not only localized at the phaseboundary but in the polymer too.
- Impedance measurements during a change of the O<sub>2</sub>-activity inside the electrolyte allow a determination of the O<sub>2</sub>-diffusion coefficient in the organic coating.

The dc-polarisation curve show:

- The speed of the corrosion reaction is controlled by the diffusion of O<sub>2</sub> through the coating to the phaseboundary metal/organic coating.
- From the diffusion limited current of the O<sub>2</sub> reduction the free, uncovered area under the organic coating could be calculated using the O<sub>2</sub>-diffusion coefficient as determined above.

SYNCHROTRON RADIATION BRAGG ANGLE CONTOUR MAPPING:  
A NEW METHOD FOR PROBING LOCALIZED STRAINS AT INTERFACES

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The high collimation and low divergence of synchrotron radiation when combined with a tunable monochromator allows probing of the localized strain fields in highly deformed materials as well as local perturbations such as at the interface strains created by thin film processing on substrates of initially "perfect" bulk crystals. Physically the entire sample surface is illuminated with a monochromatic beam tuned to an energy corresponding to the particular hkl reflection of

interest. If the reflecting planes are undistorted a uniform image of the entire surface is achieved. When distortions are present, the reflection will show contrast on the detector only in regions where the sample was in the Bragg condition subject to the energy bandpass of the monochromator. The method produces images which are maps of the field equipotentials and can be analyzed to generate all the usual properties of a three dimensional second rank tensor. The general case is illustrated in Fig. 1, which shows the equi-

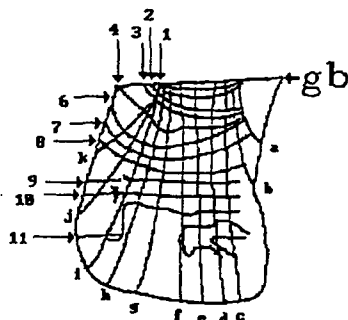


FIG. 1

potentials (1-11) and the gradient lines (a-k) on a computer enhanced image of a grain boundary nucleated crack in a fatigued zinc bicrystal.

In the case of uniform strains the equipotentials are equally spaced and the residual stress (strain) can be calculated by simply measuring the spacing between the contour lines. Fig. 2 plots the stress induced in thin film W and Mo overlays determined by this method. Thanks are acknowledged to NATO for Travel and U.S.D.O.E. for research support (to JCB).

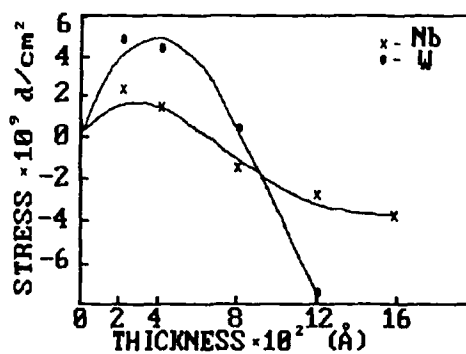


FIG. 2

**Cristallographic texture of thin films obtained by low incidence X-Ray texture goniometry.**

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The orientation of thin surface layers are necessary to be known for electronic industry as well as different studies on interphases (epitaxy, topotaxy, phase transformation, reactivity of solids...).

In the case of thin layers, the diffracted intensity is very weak and one can use the low incidence angle technics to increase the diffracting volume and, consequently, the diffracted intensity. All the information coming from the detector must be corrected.

The corrections are :

- the absorption wich depends on the thickness of the film, the irradiated area and the position of the sample,
- the new location of the information on the pole figure,
- the enlargement of the diffracted beam.

All these correction are calculated and checked on different kinds of sample : vacuum Aluminium deposits on glass, C.V.D. or P.V.D. Tungsten deposits on Silicon, P.V.D. Molybdenum deposits on stainless steel.

We have shown it is possible to obtain the texture of thin layers less than  $1 \mu\text{m}$  thick by low incidence texture goniometry ; nevertheless, one must take care on the measurement conditions and the use of a position sensitive detector would be convenient.

**The residual stresses distribution and microstructure studies in high temperature coating materials**

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The use of protective coatings in industrial applications is rapidly increasing in many new areas. The adhesive properties of the coating are of prime importance since they limit the coating's useful life. One important factor which contributes to coating failure is the residual stress produced during its manufacture.

The sources of stress-induced failure can be divided into two factors. Firstly, residual stresses present in the coating, and secondly, mechanical stresses generated during the service of the component. Although residual stress in coatings and substrates is often considered, very little written material exists concerning its actual measurement.

The generation of the residual stress in a coating depends upon different factors. For example, in the case of the plasma spray-coating process, the temperature of the sample is very important. Residual stresses may be set up during cooling following solidification due to the difference in thermal expansion coefficients between the deposit and the substrate.

This paper presents the development of a modified step-by-step hole drilling method to measure the residual stress distribution in coating materials. A finite element program has been developed to calculate the calibration coefficients for the incremental hole drilling method in the case of multi-layer materials. The main difficulty in this calculation is that of finding the elastic modulus of each coating layer material - the elastic modulus of a sprayed structure is a function of the structure's porosity and of its mechanically interlocked nature, which vary with spray parameters. The effect of the elastic modulus of the coating layer on the calibration coefficients will be studied.

The application shown is the measurement of residual stress in a NiCrAlY thermal sprayed coating and a ceramic ( $ZrO_2$ ) thermal sprayed coating. The effects of the plasma-spraying process (low-pressure plasma-spraying and air plasma-spraying) and the post-heat treatment on the residual stress distribution were studied. The microstructure in the coating layers and the substrate of the components obtained by different process were analysed. It was shown that there were some relationships between the microstructure and the residual stresses. The effect of the nature of the superalloys substrates on the distribution of residual stress will be studied.

This study shows the suitability of the modified hole drilling method for controlling the residual stress levels in coating materials. An advantage of the method is its speed, only two or three hours are necessary to evaluate the full stress gradient, thus opening up the possibility of using the method for coating process optimization.

This method can be applied to other materials with coatings thicker than 50  $\mu m$ . The method has, however, also been used to measure residual stresses, in stellite coating.

The Development of Residual Stresses  
during Spray Deposition

S C Gill and T W Clyne

The origin of residual stress development during spray deposition is explored with the help of a finite difference model which simulates the through-thickness thermal field and consequent generation of in-plane stresses.

The model refers to a single point in the spray field, but incorporates the effect of an arbitrary spray-head scan history by assuming Gaussian distributions of droplet density and gas-borne heat flux. The simulation is oriented towards conditions during powder injection into a high temperature gas torch and comparisons are made between predictions and observations made during Vacuum Plasma Spraying of ceramic, metallic and composite deposits. The model allows continuous prediction of changes in curvature of the substrate-deposit couple during spraying and quantitative comparisons are made between theory and experiment for the post-cooling curvature before and after removal of the substrate or deposit (by chemical dissolution). In addition, thermal history measurements have been made to allow selection of appropriate thermal boundary conditions.

In general, good agreement has been found between theory and experiment, confirming the dominant role played by in-plane stresses. It is demonstrated that very large stresses can readily be generated, even when substrate and deposit do not have very dissimilar expansivities, and local plastic deformation is readily generated. For ceramic deposits, it is often found that tensile stresses give rise to extensive microcracking and it is essential to simulate this effect (preferably by means of an enhanced tensile compliance) in order to obtain quantitative agreement with experiment. It is also important to monitor the deposit porosity level, which will affect the stiffness in both compression and tension. Porosity levels have been characterised in the present work via densitometry measurements. The case of composite deposits presents a complex problem, in that even if the net elastic expansivity (and other thermophysical properties) can be estimated, the large local internal stresses generated within the composite can cause complex plastic relaxation effects, which may well exhibit a significant time dependence. Methods of describing this situation are briefly discussed. Finally, some guidelines are given about the factors which give rise to coating spallation. The probable mechanisms by which bond coats can sometimes improve deposit tenacity are briefly examined and other methods of spallation control are described.

**MULTILAYER ABRASION RESISTANT PVD COATINGS**

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The paper deals with some new possibilities of producing multilayer thin coatings consisting of two metal components on the basis of titanium and tungsten coated onto the base metal matrix, mainly on tool steels or machine parts exposed extremely to abrasion and adhesive wear. Continuous formation of the so-called sandwich coatings is performed by using the PVD technology with the help of a standard equipment supplemented with an additional device the so-called sublimator. Multilayer coatings of the WC-TiC-TiN, TiC-WC-TiN and TiN-WC-TiN types were tested by X-ray diffraction, AES and SEM methods, and successfully applied to shaping and cutting tools with a tool life increase of cutting and pressing tools by 200 to 700 %.

The technology of coatings production by means of sublimator is patented, it provides broad new application possibilities.

NaCl Permeation through Polyimide Films

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Polyimides, a class of high temperature polymers, have a range of properties (high resistivity, thermal stability, chemical inertness) which make them suitable for microelectronic applications. Currently a great interest is focussed in their use as packaging material. One of the most critical properties determining device reliability and lifetime in humid and/or aggressive environment is the barrier behavior of the protective overcoat, since the ingress of moisture and aggressive species can lead to corrosion failure and alter the device characteristics. While transport properties for gases and water vapour through polyimides are available from recent literature, data concerning the permeation of aggressive ions in humid environment are lacking.

In this paper, permeability of sodium chloride through thin polyimide films (spin coated PMDA-ODA polyimide and KAPTON HN 30 films, Du Pont) in high humidity (100%) environment is investigated using a two compartment permeation cell. A highly concentrated NaCl-solution (5 M) is injected in the input side of the cell, the output side contains distilled water. The flux of  $\text{Na}^+$  and  $\text{Cl}^-$  ion through the membrane is determined by measuring the ion concentration in the output side as a function of time.

It has been found that polyimide films, both PMDA-ODA and KAPTON HN exhibit an extremely low permeability in the range of  $10^{-14}$  to  $10^{-15}$   $\text{cm}^2/\text{s}$  for sodium chloride in aqueous solution. No significant differences in the permeability for  $\text{Cl}^-$  and  $\text{Na}^+$  ions was detected. Very thin ( $2\mu\text{m}$ ) PMDA-ODA membranes showed a wide scatter of the permeability data, which was attributed to inhomogeneities and defects of the films.



WATER UPTAKE IN A CORROSION PROTECTIVE COATING SYSTEM

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For an organic coating to function well in protecting steel against corrosive attack it must adhere firmly to the steel surface. This is especially important when the coating system is exposed to a hot and wet environment. In a study of the methods to improve adhesion chemically between an epoxy coating and steel, it was found necessary to study the polymer material in isolation.

The water uptake in an epoxy-phenolic type resin at a temperature below  $T_g$  has been studied over a period of up to 50 days. Between 200 and 400 hours an increase in absorption rate is observed. Some tentative explanations for this phenomena will be presented for comment.

DSC results imply that part of the water contained within the polymer is in a crystallisable form, ie. a water melting peak is observed at  $0^\circ\text{C}$ . A reduction in  $T_g$  of  $20^\circ$  is observed with a water content of 6%. This supports the observation that part of the water does not contribute to plasticisation. The DSC measurements are complimented by Dynamic Mechanical Thermal Analysis (DMTA) results.

Water content is correlated with adhesion measurements made by a direct pull-off test of the coating on a polished steel surface. It is reported that at very low water content of the polymer, the pull-off strength is greatly reduced. Comments are made relating to the adhesion improvements provided by chemical modification of the polymer-metal interface.

**Effect of the Uniformity of Al-Si Sputtering Targets on their  
Sputtering Behaviour**

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Produktion und Logistik

As the silicon technology advances toward VLSI, the trend of device miniaturization continues to demand an increase in the performance of thin-film interconnects. This gives rise to requirements for a high uniformity of the Al-Si sputtering targets. The present work studies the effect of inclusions in the sputtering target on its sputtering performance and on the uniformity of the metallization. The results indicate that inclusions in the target are transported during the sputtering process as fragments to the wafer surface. These fragments which are incorporated into the metallization can cause defects in the lines. A simple method for determining small amounts of inclusions is presented.

Deposition of Polycrystalline  $\text{In}_2\text{S}_3$  on Modified Polyaniline Substrates

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$\text{In}_2\text{S}_3$  is known for its photoinducting properties and it is used in photocells alone or in combination with Cu, Zn and Cd sulfides. Polyaniline (PA) is a conducting polymer with conductivities approaching those of metallic conductors, behaving as a p-semiconductor. As such it may be used for the construction of photovoltaic elements. It has recently been found that the conductivity of PA increased upon treatment with chlorosulfuric acid, which results in introduction of  $-\text{SO}_3\text{H}$  groups in the PA polymers. The presence of these groups are likely to favour the deposition of sulfides on the polymer. In the present work, we report on the ability of sulfonated PA substrates to induce  $\text{In}_2\text{S}_3$  precipitation from aqueous solutions, supersaturated with respect to this phase.

Sulfonated PA substrates with degrees of sulfonation 10%, 30% and 50% and conductivities of 3.2, 3.9 and  $5.7 \text{ S cm}^{-1}$  were introduced in supersaturated aqueous solutions, made by mixing equal volumes of  $\text{InCl}_3$  and  $(\text{NH}_4)_2\text{S}$  at  $25^\circ\text{C}$ . The pH of the solution was adjusted at 2.0 by the addition of standard HCl. Following the lapse of induction periods, inversely proportional to the solution supersaturation, precipitation started and it was monitored by the change of the solution conductivity. The rates of  $\text{In}_2\text{S}_3$  deposition, which was verified as the only phase forming, were proportional to the solution supersaturation. On the basis of the kinetics results it is suggested that the deposition of Indium sulfide occurred at the sites provided by the  $\text{SO}_3\text{H}$  groups of the polymer.

SiO<sub>2-x</sub> Coatings on Polyester Films: Preparation and Properties.

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SiO<sub>2-x</sub> coatings on polyester films may be used for food packaging, where they offer transparency in combination with good barrier properties towards oxygen and water vapour permeation. The present paper introduces the method used for the coating and characterizes the films prepared: The structure of the film is investigated by TEM methods, further the permeation rate and the mechanical properties are revealed and discussed with respect to the application. The oxygen deficiency is characterized by the transparency using a photospectrometer.

A NEW METHOD FOR STUDYING ACCELERATED AGEING OF INTERCONNECTION MATERIALS  
APPLIED TO THICK FILM RESISTORS.

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A new method, referred to as the in-situ method, is described to study accelerated ageing of materials used in interconnection technology. The method is based on measuring the resistance drift continuously during accelerated ageing of the material at an elevated temperature, whereas in traditional ageing experiments the resistance drift is measured at room temperature after subsequent ageing steps at an elevated temperature. The in-situ method presented here allows a measuring resolution for the electrical resistance in the order of a few ppm, which is orders of magnitude better than the resolution usually obtained in classical ageing studies. This high resolution allows not only to measure small resistance changes (10 to 1000 ppm) induced by ageing processes, but also to study accurately the kinetics of the processes involved. Since for most materials used in interconnection technology resistance changes in the order of 1000 ppm can be induced by accelerated ageing during a few days, the time required for ageing studies can be drastically reduced by this new method.

In this paper we demonstrate the applicability of the method to the ageing of high stability thick film resistor systems like the Du Pont HS 80 system. High resolution resistance drift data are presented on Du Pont HS 8021 (100Ω/□), HS 8031 (1 kΩ/□) and HS 8049 (100 kΩ/□) test patterns. The glazed and trimmed test patterns were aged at temperatures up to 190°C in a pure helium atmosphere. A careful analysis of the ageing kinetics leads to the conclusion that the resistance drift is not caused by a single ageing process with a sharply defined activation energy, but rather by a spectrum of processes, distributed in activation energy. This is rather surprising, since classical ageing studies did not reveal the existence of such a spectrum. It is suggested that the ageing mechanism is related to structural relaxation of the amorphous dielectric matrix of the resistor. A mathematical model is presented to describe the kinetics of ageing induced by a spectrum of processes. Some practical applications with respect to long-term drift and lifetime prediction are discussed.

ACCURATE MEASUREMENTS AND INTERPRETATION OF RESISTANCE CHANGES IN OFF-CHIP  
INTERCONNECTIONS DUE TO AGEING IN AN INERT GAS ATMOSPHERE.

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Classical reliability and ageing tests in micro-electronics are in general long term experiments (e.g. storage tests at high temperature, 85°C/85% r.h. storage tests, pressure cooker tests ...). Therefore, it usually takes a long time before a device can be taken into production. So there is a need for methods that are able to identify ageing mechanisms in a shorter period of time.

In another paper presented at this conference [1], a new method - referred to as the in-situ method - to study accelerated ageing of materials used in interconnection devices, is described. The in-situ method is based on measuring the resistance change of a component at the ageing temperature with high resolution, so that the kinetics of the ageing process(es) can be derived from accelerated ageing behaviour on a short time scale (typically a few days).

In this paper we discuss results obtained using the in-situ method on inert-gas ageing of several types of off-chip interconnections :

- 1) Au and Cu ball bond contacts on Al-metalisation : It is shown that the dominant ageing process is diffusion driven. For the case of Au ball bonding, diffusion leads to the formation of Kirkendahl-voids, which finally results in crack formation and failure of the bond contact. Effective activation energies for ageing of both Au and Cu ball bonds are derived, and are in good agreement with literature results.
- 2) Au, Cu and Al-Si wires used in bonding applications : for 30  $\mu\text{m}$  diameter wires used in bonding applications, the dominant ageing process is the annealing of defects introduced during fabrication of the wire. It is shown that the annealing processes can be distributed over a large range of activation energies, so that an Arrhenius type analysis is not applicable. A kinetic model incorporating a spectrum of activation energies is therefore used in the analysis of the data.

These results show that, using the in-situ method, it is possible to identify ageing processes in off-chip interconnections and to analyse their kinetics on a short time scale.

[1] L. De Schepper, L.M. Stals, R. Vanden Berghe, S. De Molder, this conference.

## POTENTIAL DISTRIBUTION ON THIN CARBON FILMS INVESTIGATED BY A STM

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A large scale bender-STM (similar to Muralt & Pohl's /1/) is used to monitor the topography and the potential distribution of thin carbon films under current flow. The dc component of the ac tunneling current was zeroized with an external voltage equal to the potential difference between tip and sample. The voltage resolution is shown to be few per-cent of the tunneling amplitude.

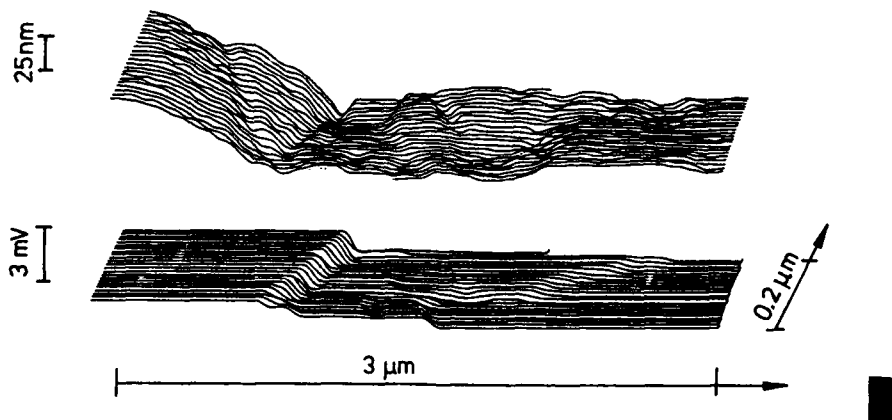
The Carbon films of Bradley-type showed in the topographic image a micro-scopic rough surface consisting of assumed graphitic clusters building large grains.

The potentiographic image contains flat areas and steps i.e. poor electri-cal connection at grain boundaries. The sheet resistance is determined by these intergrain resistances and may be treated as a percolative system.

/1/ P. Muralt, D. W. Pohl, App. Phys. Lett. 48, 514 (1986)

Topography (a) and potential distribution (b) of a thin carbon film

$U_T = 7 \text{ mV}_{pp}$ ;  $I_T = 1 \text{ }\mu\text{A}_{pp}$



**Determination of Mechanical Stresses in Plastic Encapsulated Chips  
by X-Ray Diffraction**

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In plastic encapsulated chips thermal stresses induced by temperature excursions during molding or soldering processes respectively can result in micro-cracking of the silicon chips. In order to increase the performance of such devices, special test chips containing sensors are encapsulated and the mechanical stresses are measured. However, until now no method is available for controlling the devices during the manufacturing process.

In this paper a non-destructive method is presented for determining mechanical stresses also in non-sensor chips. Therefore x-ray diffraction analyses are performed on the silicon in encapsulated chips. For a chosen reflection the shift due to bending is determined. The stress distribution in the chip can be calculated.



Electromigration - microstructural investigation, failure analysis and  
life time measurements

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The material transport mechanism by diffusion under the driving force of the electron wind of an electrical current is called electromigration. In thin film metallisation interconnections of VLSI-circuits electromigration is the dominant failure mode.

A investigation of the microstructural parameters of various metallisations (different in alloy additions and production history) such as the surface roughness, the microhardness, the grain size and the distribution of the alloy elements before and after the electromigration test demonstrates the sensitivity of this thin film properties and their electromigrational behaviour on the sputter- and temperconditions as well as on the substrate and passivation materials.

The electromigration stability of the metallisations are measured on wafer level under accelerated conditions. The use of different test-temperatures and current densities allows a calculation of the parameters influencing the electromigration.

Both, the median time to failure (MTF) results and the microstructural and chemical analysis were used to understand the influence of alloy additions like titanium and copper and to optimise the production parameters of the integrated circuits.

## The dielectric strength of AlN-ceramics

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In addition to its very good thermal properties (thermal conductivity  $\lambda \geq 150 \text{ W/m} \cdot \text{K}$ ) AlN-ceramics have a relative low dielectric constant ( $\epsilon \simeq 8.6$ ) and a high dielectric strength ( $DS \geq 20 \text{ kV/mm}$ ). The combination of these properties allows the use of AlN in high performance electronics.

AlN-powder (H.C. Starck, grade A) was mixed with different additives ( $\text{Nd}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ), attrition milled and pressureless sintered at temperatures between  $1850^\circ\text{C}$  and  $1950^\circ\text{C}$ . The dielectric strength of various samples with different thickness was detected (non-destructive high voltage insulation tester JP 30A, Danbridge, max. output 30 kV). The damage of the samples and the discharge path were observed by REM. The mechanical and dielectric strength were compared and specified by Weibull statistics.

It is shown that the dielectric strength of AlN-ceramics depends on the electric potential  $U$ , the duration of the load application  $t$  and the derivative  $dU/dt$ . The resulting discharge channel usually goes through regions with a certain discontinuity in the dielectric constant (electric field amplification by polarization at pores, triple points filled with glass phase, ...). In contrast to the observed branching of discharge channels in gases, fluids and polymeric materials one cannot find such a branching in AlN-ceramics. There is only one channel running through the sample with a diameter of  $10 - 25 \mu\text{m}$ , which is much bigger than the average diameter of AlN-grains. The damaged region at the sample's surface is 2 - 5 times bigger than the hole of the discharge channel.

STUDY OF NEW SOLID SUPERIONIC MATERIAL  $Ag_7P_3S_{11}$

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The conductivity of a new superionic material  $Ag_7P_3S_{11}$  has been studied in the temperature range of 25 °C-80 °C, the latter being its dissociation temperature. At 25 °C, its conductivity is found to be 0.29eV through Nernst Einstein plot. The study indicates that the material has an average structure and the disorder factor seems to be 2.7. The ionic transport number is almost unity.

INVESTIGATION ON GROWING OF SEMI-INSULATING UNDOPED AND ISOELECTRONICALLY DOPED GALLIUM ARSENIDE OF THE DIAMETER OF 76MM FOR HIGH SPEED INTEGRATED CIRCUITS

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Investigation on the growing of semi-insulating crystals of GaAs of the diameter of 76mm has been carried out aiming at meeting the requirements of microelectronics for the preparation of integrated circuits of high speed and integrity.

A comparison of the methods of growing of that material has been done to find out the way of improving its structural and electrical properties. Special attention was paid to the growing of isoelectronically doped single crystals by the method of Czochralski for reducing the dislocation densities and improving the homogeneity of the crystal. A number of technological parameters of the process of growing as rate of growing, rotation of the crucible and seed, amount of the charge and chamber pressure were studied in relation to the yield of single crystals and their electrical and structural properties.

Some aspects of the influence of heat treatment in connection with the mechanical and electrical parameters of the grown up crystals were observed.

# STRUCTURAL AND MAGNETIC STUDY OF HIGH COERCIVITY AS-CAST RARE EARTH-IRON ALLOYS FOR PERMANENT MAGNETS

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In the last few years the discovery of high energy magnets based on tetragonal RE-Fe-B (RE= rare earth) compound has strongly stimulated the search for both new RE-Fe high anisotropy phases and the development of low cost processing.

We have focused our attention on two systems which develop high coercivity in as-cast polycrystalline bulk materials: Dy-(Fe,Co)-(B,C) and  $\text{Nd}_{100-x}\text{Fe}_x$  (with  $2.5 \leq x \leq 20$ ) intermetallic alloys.

The main interesting features of the ternary carbides in which the hard magnetic phase is isostructural with the 2:14:1 borides is the difference in its microstructure and phase formation mechanism. Combining an accurate X-ray diffraction analysis, Mossbauer spectroscopy and magnetic measurements, we found that: i)  $\text{Dy}_2\text{Fe}_{14}\text{C}$  is formed from a C doped  $\text{Dy}_2\text{Fe}_{17}$  phase as precursor; ii) strong microstructural differences respect to borides are present in the composition range  $\text{Dy}_{15}\text{Fe}_{77}(\text{B}_{1-x}\text{C}_x)_8$  (with  $x \geq 0.5$ ) with consequent increase of the coercive field (for  $x=1$ ,  $iH_c=17$  kOe); iii) replacing Fe by Co, an increase of Curie temperature occurs (for Co content= 0.5,  $T_c=675^\circ\text{C}$ ).

For the as-cast  $\text{Nd}_{100-x}\text{Fe}_x$  alloys the existence phase region and the anisotropy field of the new "oxygen stabilized" phase are reported. In conclusion: i) for  $x > 20$ , i.e. for an increase of Fe content, the  $\text{Nd}_2\text{Fe}_{17}$  compound appears with consequent abrupt decrease of the coercive field; ii) the new hard magnetic phase shows a Curie temperature value of  $245^\circ\text{C}$ , a room temperature anisotropy field of 19.5 kOe and, for  $x=20$ , the as-cast alloy has the highest coercive value of about 4.5 kOe.

**R.T. SPUTTERING OF Bi-SUBSTITUTED GARNET FILMS  
FOR THERMO-MAGNETO-OPTICAL RECORDING**

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Bi-substituted garnet films are very promising for magneto-optical recording because of their strong magneto-optical activity and high chemical stability [1]. Using glass substrates,  $(\text{BiY})_3(\text{GaFe})_5\text{O}_{12}$  or  $(\text{BiDy})_3(\text{GaFe})_5\text{O}_{12}$  amorphous films have been prepared by facing target sputtering [2]. Sputtering in  $\text{Ar-O}_2$  mixture instead of pure Ar improves the Bi-substitution which then becomes very close to the targets' one. Post-annealings are necessary in order to crystallize these films which are then polycrystalline with no preferential orientation. They exhibit Faraday hysteresis loops with high coercivity which depends on the oxygen partial pressure. The perpendicular magnetic anisotropy is stress induced. The films have a large Faraday rotation, typically  $5.10^4$  deg/cm at  $\lambda = 500$  nm. A static recording experiment has been performed on these films coated with a chromium layer.

- [1] M.GOMI, T.TANIDA and M.ABE, J.Appl.Phys. 57, 3888 (1985)
- [2] M.MATSUOKA, M.NAOE and Y.HOSHI IEEE Trans.on Mag. MAG 21, 1474 (1985).

## Electrical Conductivity of Chromium(III) Oxide

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The oxide,  $\text{Cr}_2\text{O}_3$ , is a semiconductor that is highly resistant, refractory (2673K) and antiferromagnetic ( $T_N = 60\text{K}$ ). Due to high electrical conductivity, it also signifies many of the requirements for the high temperature electrodes in MHD power generation, high temperature fuel cells and catalytic combustion. In our present investigation, the dc electrical conductivity of sintered pure  $\text{Cr}_2\text{O}_3$  and doped with  $\text{MgO}$  and  $\text{La}_2\text{O}_3$  have been studied by employing a standard four-probe technique in the temperature range 300 - 1400 K in different atmospheric conditions ( $p_{\text{O}_2}$  ranging from 1 to  $10^{-14}$  atm.). Plots of  $\log \sigma$  vs  $1/T$  follows straight lines but with three different slopes in three different temperature ranges. The activation energies obtained by the least square methods were  $8.0 \text{ kJ mol}^{-1}$  below 500 K,  $60.0 \text{ kJ mol}^{-1}$  between 500 - 900 K and once again decreases to only  $3.0 \text{ kJ mol}^{-1}$  at still higher temperature. The data suggest that in the low temperature range, grain boundary conduction plays an important role, while at high temperature, it may be due to annealing of excess Cr-vacancies. In the high  $p_{\text{O}_2}$  region, the conductivity gives rise to a p-type conduction for pure  $\text{Cr}_2\text{O}_3$  specimen and for  $\text{MgO}$  and  $\text{La}_2\text{O}_3$  doped specimen, the conductivity remains independent throughout the whole  $p_{\text{O}_2}$  range indicating an intrinsic conductivity arising from a stoichiometric defect situation.

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DISPERSION STRENGTHENING IN HIGH TEMPERATURE MATERIALS -  
PRINCIPLES FOR ITS OPTIMIZATION COMING FROM NEW THEORETICAL  
CONCEPTS

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Dispersion hardening is an important strengthening mechanism utilized in many high temperature materials. It is the aim of this paper to give guidelines as how to maximize this strengthening contribution by choosing suitable dispersoid-types and -sizes. These guidelines are based on recent developments in the theoretical understanding which lead to a new constitutive creep equation (1,2).

Firstly, the proper choice of the dispersoid type is important. Particles which exert a strong attractive force on moving dislocations are needed to ensure high creep strength. It will be shown that direct information about this interaction strength can be obtained from the shape of the creep curves. Thus alloy-screening becomes possible in the sense that favourable dispersoid/matrix combinations can be identified from a limited number of creep tests. This will be exemplified for dispersion strengthened aluminum alloys and Ni-base superalloys. Possibilities for further improvement of the creep strength will be outlined.

As a second parameter, the particle size at given volume fraction influences the creep strength. It will be shown that an optimum particle diameter exists. How alterations (refinements or coarsening) of particle sizes in dispersion strengthened materials should affect the creep strength will be discussed.

1.) J. Rösler, Fortschr.-Ber. VDI Reihe 5 Nr. 154, Düsseldorf, 1988

2.) J. Rösler und E. Arzt, zu veröffentlichen

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XII.2

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The Stress Exponent of Particle-Strengthened Alloys

poster  
withdrawn!

INTEREST OF A REINFORCEMENT BY COHERENT PARTICLES  
TO OBTAIN A COPPER ALLOY WITH  
HIGH ELECTRICAL AND MECHANICAL PROPERTIES .

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From a solid solution Cu- 0.25% at Al, it is possible to obtain, by internal oxidation, an O.D.S in which the particles are coherent with the copper matrix. The composition of these particles is different of alumina composition, but is almost the same as this of a double oxide CuAlO. The particle-matrix coherency ensure a larger reinforcement than the one obtained with stoichiometric oxide, even for a weak concentration : more the reinforced alloy keeps a high electrical conductivity.

These particles with a coherency contrast are observed by T.E.M. and a weak-beam study clearly prove that they have a spherical form. Their crystalline structure is determined by a numeric simulation after recording X-rays diffusion near Bragg reflections :

1-the spherical form observed allow the theoretical calculation of the diffusion by means of an elastic model

2-comparing the theoretical and observed diffusion curves, it is possible to determine the structure factors  $F_{hkl}$  of the coherent particles.

The values of  $F_{hkl}$  are those of a CuAlO spinel compound. The transformation of the coherent particles CuAlO in incoherent particles  $Al_2O_3$  occurs by a mechanism of throwing out the Cu atoms when coherent particles reach some critical size .

These results allow an estimation of the optimum size for the powder to be utilized in making copper alloy with good mechanical and electrical characteristics, by means of powder metallurgy .

THE TEMPERATURE AND THE THERMOELASTIC STATE IN AN INFINITE  
MATRIX CONTAINING A PARTLY UNBONDED RIGID FIBER

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The plane problem of heat conductivity and thermoelasticity is considered for a plate containing a rectilinear, thin-walled inclusion of finite length, which is perfectly bonded along one of its faces to plate, while its other face forms a crack.

The temperature field in the infinite elastic plate and inclusion is determined using the complex formulation of the problem of the heat conduction. Based on the thermal contact conditions between the inclusion and the surrounding material the temperature field is obtained in terms of two piecewise holomorphic functions.

The thermoelastic problem is studied using the complex variable technique. Based on the conditions of the matrix-inclusion interface and the crack, and using the temperature field which was found above, the boundary problem is reduced a Hilbert problem of the complex variable to theory and a closed form solution is obtained.

The complex stress intensity factor for stress singularities is defined and the local stress distribution in the neighborhood of the crack tips is given. In this problem a different singularity of the stresses to the well-known singularity is observed. The order of this singularity is 0.75.

AN OVERALL SCHEME FOR THE RESOLUTION OF THE CREEP/FATIGUE INTERACTION PROBLEM UNDER THERMOMECHANICAL LOADS.

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This paper concerns with the problem involved when a non elastic material is placed under push-pull thermomechanical load conditions. In many situations where the temperature is involved this is time dependent, and it must be considered in a creep/fatigue problem. There are six aspects to be solved when analyzing questions here placed: temperature distribution  $T(x, y, z, t)$ ; material behaviour, stress and strain distribution  $\sigma(x, y, z, t)$  and  $\epsilon(x, y, z, t)$ ; creep/fatigue interaction for lifetime prediction; experimental test and programme computer including the previous five. This paper gives a guideline attempt for these questions with exact solutions from mathematical point of view.

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Simulation of internal tension, structure and mechanic properties

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Thermal stress is a result from different cooling and heating conditions. This stress is often overlayed by external forces and leads sometimes to the destruction of a body.

Generally the basic equations of elasticity and plasticity cannot be solved in an analytic way. With the help of the finite-element-method it is possible to calculate the deformation and the stress of a real body by any external force and any temperature condition.

Physical problem

In order to enable the calculation of stress with the help of the finite-element-method, the 2-D geometry is divided into small (finite) triangles.

On the assumption that the tension within such a triangle is constant and that it consists of linear elastic-plastic material behavior, the stress of an element can be calculated out of the tension. With the principle of virtual power one gets the forces in the knots of every triangle. The sum of all forces in every knot has to be equal zero.

In this way the problem of stress calculation can be reduced to a linear set of equations.

## CRACK NUCLEATION AND PROPAGATION IN ZINC BICRYSTALS

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Studies of crack nucleation and propagation at both room Temperature and 77K have been made on high purity zinc bicrystals as a function of relative orientation and degree of prior tensile or fatigue deformation. The bicrystals were so oriented that, in general, one grain (CrI) had its basal normal parallel, or closely parallel, to the tensile axis. Plastic deformation begins in the second grain (CrII), oriented by relative to CrI by a simple tilt, twist or combination of the two. The constraint imposed by CrI leads to non-basal slip in a region, the boundary affected zone (BAZ), adjacent to, and incorporating, the grain boundary. Cleavage cracks were always nucleated in this BAZ in CrII, at stress levels below those for similarly oriented single crystals. Prior fatigue deformation can further lower the stress at which crack nucleation occurs. At room temperature the following sequence of events, each taking place at a successively higher stress, is observed: (i) multiple slip at the grain boundary leading to formation of the BAZ (ii) nucleation of a crack in the BAZ (iii) extension of the crack across the BAZ in CrII (iv) extension of the crack across the entire section of CrII (v) propagation of the crack into CrI and subsequent failure of the bicrystal. At 77K crack nucleation is usually followed by total failure with no increase in stress. For bicrystals whose two grains are related by a simple tilt, crack propagation across the boundary is subject to some slight hindrance, and the stress required is somewhat greater than the value expected for propagation in a homogeneous single crystal. When a twist component is present in the relative orientation of two grains, crack propagation is accompanied by tearing at the boundary and large, regularly spaced cleavage steps on the fracture surface of CrI. The stress to propagate the crack is now several times that for a crack in a single crystal. When CrI is so oriented that basal cleavage is suppressed, non-basal crack propagation is accomplished by a mixture of twinning and cleavage, at even higher stress levels than required for propagation across a twist boundary. The implication of these findings is that, in the absence of any surface defects, fatigue cracks in polycrystalline materials are nucleated at the first internal grain boundary.

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science, under contract no: DE-FG 03-88ER45350, and the international collaboration was made possible by the award of a NATO Exchange Travel Grant.

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## THE ORIENTATION OF GRAIN BOUNDARY PLANES IN POLYCRYSTALS

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The existence of 'special' interfaces whose properties deviate markedly from average has been known for some time. The question then arises, how this phenomenon might be exploited to engineer materials so as to contain increased proportions of those special boundaries which confer beneficial properties. This concept is encapsulated in a new branch of materials science known as 'grain boundary design'. Implicit in this is the requirement that special boundaries can be readily identified. As yet however, the relationship between boundary structure and physical properties are only poorly known. Real progress towards the goal of grain boundary design can only be made when those boundary geometries which give rise to special properties can be identified.

The coincident site lattice (CSL) model is one method for categorisation of interfacial geometry. However, it is now accepted that a high value of coincidence lattice sites between two adjoining crystals does not necessarily lead to their interface possessing special properties, though it is far more likely than a non-CSL type. The inadequacy of the CSL model is that it takes no account of the orientation of the boundary plane between the crystals and thus the degree of coincidence or atomic density within the boundary itself.

The most successful experimental technique for measuring grain misorientations is 'Backscatter Kikuchi Diffraction' (BKD) applied in a scanning electron microscope. This technique allows rapid measurement of grain misorientations in bulk specimens by on-line computer analysis of the patterns. Recently, in the light of the additional importance of the boundary plane orientation the BKD technique has been extended to include this measurement as well. The method relies on observing the grain boundary trace on two surfaces, from one of which the grain orientations have already been measured using the BKD technique. It is preferable though not essential to prepare the surfaces at right angles to each other. The boundary plane orientation is then calculated in terms of the orientations of both neighbouring grains and a computer search made to establish whether it lies parallel to any special plane.

Along with the development of the BKD technique has been the formulation of a method of obtaining grain boundary normals using transmission electron microscopy. By measuring both the foil thickness and the boundary inclination and knowing the orientations of the adjacent grains the orientation of the boundary plane can be determined. Both the BKD and TEM techniques provide the same information. However, the BKD technique has been shown to be far quicker for the collection of statistically significant amounts of data. The TEM technique does however allow the defect structure or microfaceting at the interface to be analysed at the same time and in certain circumstances may be the preferred method.

Although quite a high proportion of CSL misorientations were observed in our study it was rare for the boundary plane to coincide with the most densely packed plane in the CSL. For example, in a just recrystallised stainless steel specimen, only 3% of sampled boundaries were near a symmetrical tilt configuration. Asymmetric tilts were more common (11%), but the most preferred boundary geometry was for the boundary plane to be close to low index crystallographic directions in both grains (29%).

XXIII.2

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Experiments on Material Distribution Analysis with a Scanning Tunneling Microscope

poster

withdrawn!



Development of a new CW&BP - process for specialty steels and superalloys

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For special high alloyed steels, tool steels, high speed steels and superalloys continuous casting and hot working in one heat is possible only with horizontal continuous casting (HCC) of close to final section (CFS) bars and wires so, that the deformation ratio is not higher than minimum needed to achieve required properties of the product.

The known employment of horizontal continuous wire and bar caster for nondeformable materials gained with this aim the new near net shape importance in the shortening of technological procedures for wire and bar production.

The most important problem in the industrial development is connected with know how to cast small sections from existing large melting furnaces.

Induction heated tundish, holding the melt with controlled ferrostatic pressure and argon purging is the most suitable for smaller production units. For larger ones instead of induction heating a new electro slag heating (ESH) proces has been developed and practically first introduced in the MIL pilot plant.

This process is of special interest for holding the melt longer time at controlled temperature and pressure with refining going on what is important for HCC of smaller sections and for slow continuous atomisation process of molten metal in powder metallurgy.

This proces at the same time enables the production of larger ingots and castings from smaller melting furnaces, assuring special quality of products trough finer solidification structure.

The new flexible pilot plant at Metalurški Inštitut Ljubljana, is the first in the world dedicated completely to the development of a new compact wire and bar production (CW&BP) process:

- vacuum induction melting furnace
- induction heated pressure holding furnace with argon purging
- first existing experimental unit for the newest electro slag heating process with Ar-purging
- complete computer controlled three strand wire and bar caster adjustable for the dimensional range from  $\varnothing$  2,6 mm to 40 mm
- controlled cooling, adjusting and hot coiling/decoiling unit
- forging machine for maximal input  $\varnothing$  40 mm and min. output  $\varnothing$  8 mm
- hot drawing and Properzi-cold rolling from  $\varnothing$  8 mm to  $\varnothing$  2 mm.

Additionally for flexibility there are abilities for electro slag remelting, water atomisation and HIP for PM technology, rapid cooling and ribbon pulveriser units in this pilot plant.

"CHROMIUM AS A NOVEL HIGH TEMPERATURE MATERIAL"

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As for other refractory metals a purity of 99,96 weight-percent chromium is considered as technically pure. This purity can be achieved using melting or powder metallurgical methods. High purity chromium can be fabricated to semi-finished and finished products such as large plates, tubes, rings and different containers. Maximum dimensions possible depend on method of fabrication and equipments used. The most economic way to produce such parts are powder metallurgical methods. Based on this production methods dimensional limitations will be discussed. The classical powder metallurgical way of production will be described, concentrating on the following main production steps:

- Fabrication and treatment of powders
- Cold isostatic pressing
- Sintering of pressed parts and
- Forming operations for sintered chromium

Examples of finished parts fabricable from semi-finished sheet or rod will be presented. The last chapter summarizes basic data for physical and mechanical properties together with chemical properties of wrought chromium.

# A New Apparatus for Combined PVD and Ion Implantation of Thin Films

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Ion implantation and ion mixing techniques are very effective to produce thin surface layers with well defined, predetermined composition. It is possible to obtain not only stable phases, but also metastable, or glassy ones, which extend well beyond the thermodynamic equilibrium limits and present unique physical and chemical properties. However the inherent shallow thickness of the treated layers constitutes a serious drawback for their practical use.

A combination of ion treatment with another physical vapour deposition technique, e.g. evaporation, or sputtering, constitutes a powerful alternative, which allows for producing much thicker coatings, yet maintaining the advantages of ion bombardment. Moreover, ion beam assisted deposition requires lower ion energies, in the keV, or tens of keV range, than conventional implantation, or ion mixing, which need energies of the order of hundreds of keV, or MeV. Indeed the hybrid process consists of deposition and implantation steps, which may be simultaneous, or sequential, the depth of the treated region being nearly independent on the projected range of the implanted species. The combination of process parameters such as gas pressure, evaporation rate, ion energy and dose significantly affects film composition and properties. Unusual structural properties are observed, as well as improved mechanical (uniformity, hardness, adhesion to the substrate) and chemical ones in materials ranging from metallic to ceramic coatings.

In this paper the design and preliminary performance data of a new machine which allows the formation of multicomponent ion beam assisted coatings are described. The apparatus consists of a Duo-plasmatron ion source, a mass analyzer, a target chamber adaptable for use with various samples up to 10 cm in diameter, and a 2-crucible electron gun evaporator with film thickness monitor. It has been conceived with a high degree of process automation.

The hybrid technique combines some of the better features of both, co-deposition and implantation to produce surface alloy layers with a high control of microstructure and properties. Homogeneity of the formed films and their adherence to the substrate are highly improved with respect to those of samples obtained by conventional implantation or deposition alone.

High Temperature Deformation of Quenched and Aged  
Al-5.8%~~Mg~~ Alloy

By

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Mechanical properties of as quenched and aged Al-5.8%~~Mg~~ alloy for 24h at 393K and 433K has been investigated in the temperature range of 300 to 700K to assess the effect of aging temperature on deformation in presence of precipitation. The results indicate that, at constant strain rate, the ductility increases with test temperature reaching a maximum value and then decreases to minimum value followed by an increase at higher temperatures. The temperature corresponding to the minimum ductility, the elevated temperature 0.2% yield strength and ultimate tensile strength were found to be depend on the starting material conditions. The variations in the yield and ultimate tensile strength, parabolic stress-strain relationship and work hardening index of flow were recorded as functions of experimental variables. Electron microscopy revealed the presence of different shapes of  $Mg_2Al_3$  precipitates whose size, quantity and morphology depended on the experimental conditions. An attempt has been made to correlate strength, ductility and structural changes at elevated temperatures.

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Study on Thermal Diffusivity of Carbon Aluminium Composite

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The thermal diffusivity of carbon fibre-aluminium composite has been measured using Laser pulse technique. The specimen was prepared by squeeze-casting method and contained 0.156, 0.244, 0.509 volume fraction of carbon fibre respectively. The carbon fibre is randomly arranged and there is no obvious difference in orientation between the specimen. The experiment was carried out from 150°C to 500°C in nitrogen gas atmosphere.

The results show: When the carbon fibre volume fraction increases from 0.156 to 0.244, the thermal diffusivity of the composite does not decrease obviously and even increases somehow. While the carbon fibre volume fraction further increases to 0.509, the thermal diffusivity decreases significantly. The thermal diffusivity data of the first run and the second run for the composite containing 0.156 and 0.244 volume fraction of carbon fibre are about the same, but for the composite containing 0.509 volume fraction of carbon fibre, the differences between the first run and the second run are quite big. This phenomenon may be mainly contributed to the crack and delamination of the composite during heating.

Such explanation is supported by the observation with microscopy and the measurement of the porosity of the composite. After having been measured the thermal diffusivity, the specimen were etched with dilute mixture of hydrochloric acid and nitric acid and it can be observed clearly that the more carbon fibre the composite contained, the more serious delamination appeared. The measurement results of porosity show that the porosity percentages of the composites are 0.718, 1.274 and 9.33 corresponding the composites contained carbon fibre volume fraction 0.156, 0.244 and 0.509 respectively. The latter is much bigger than former two.

# Production of Sintered Porous Aluminium Materials

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The production of high porous, permeable sintered materials is a monopoly of powder metallurgy techniques. They are produced from a great variety of metals and alloys. Of great quantitative significance are Bronze, Stainless Steel, Nickel and special alloys like Hastelloy®, Inconel®, Incoloy® and Monel®. However, even today there is not one particularly satisfactory method to obtain aluminium material with high porosity. For this reason, experiments were carried out to produce porous Al materials through gravity sintering method.

Gravity sintering of Al alloys with high strength matrix could not be carried out due to  $Al_2O_3$  film formation on the surface of the Al powder, that inhibits the neck formation in liquid phase sintering. Through intense milling of Al powders along with the addition of selected metal powders, sintering could be activated and compacts possessing satisfactory strength and permeability were obtained. This specially prepared porous Al materials possess an uniform and continuous porosity, with predictable properties and promise future application for light and corrosion resistant filters. Porous metals find wide applications in heat transfer control, fluid conditioning, handling of bulk materials, friction control, sound and impact absorption, etc...

Porous Al-materials fill the lacunae in the spectrum of properties of metallic materials connecting relatively high strength with low density. This presents the new state of art of the production of sintered Al-materials.

The Prediction of Crystal Structure By Molecular  
Packing Analysis

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As the first step of a priori prediction of organic crystal structure, the project was started by assuming that a space group information can always be obtained from experimental source such as powder diffraction. The key program used was SUMPAC which is based on molecular packing analysis(A.I.Kitaigorodsky, Molecular Crystals and Molecules, Academic Press, 1973). A known structure of Tetranitro-tetraazacyclooctane (C.S.Choi and H.P.Boutin, Acta Cryst., B26, 1235(1970)) was used to test the method. The molecular conformation was taken from C.S.Choi, et al., and fixed throughout the procedure. Judged by both packing efficiency and energy, SUMPAC found the most probable structure which was in turn refined by WWMIN, a program to model molecules and crystals in terms of potential energy functions (William R. Busing, ORNL-5747, Oak Ridge National Lab, TN 37830, 1981). The final cell dimensions and lattice energy calculated were essentially the same as the real ones within the experimental errors. The work was supported by the Science Foundation of China under contract No. 2870144.

- (a) Dechun Zhang, Department of Chemistry, Suzhou University, Suzhou, P.R.China 215006
- (b) The prediction of crystal structure
- (c) Poster session

PO 08

Double-gradient approach  
in non-linear thermoviscoplasticity

by

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and

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This paper deals with the shear stability and localization of a non-hardening thermoviscoplastic slab subject to a steady shear stress applied on the top, with the bottom of the slab kept fixed. The new element in this approach is the inclusion of higher-order strain gradients in the constitutive law for the stress [Aifantis, The Physics of Plastic Deformation, Int. J. Plasticity, 3, 211-247, 1987], which expresses the influence of the microstructures via phenomenological coefficients. We show that the inclusion of the second-order gradient plays a stabilizing role, by smoothening out the non-uniformities in strain and temperature distribution.



**Constitutive Modeling of Primary and Secondary Creep of  
Single Crystals at High Temperatures**

**by**

**Albrecht Bertram, Diego Lozano, Jürgen Olschewski,  
Mirjana Zelewski (BAM, Berlin)**

In order to describe the primary and secondary creep behaviour of single crystal superalloys, a constitutive equation in form of a second order differential equation in time from linear viscoelasticity theory is suggested. By means of a numerical optimization strategy the material constants have been adopted to cyclic creep test results. The three-dimensional version of the model reflects the full symmetry of the f.c.c. single crystal. Each of the remaining 12 material constants has a specific physical interpretation. Their numerical range can be determined in order to assure consistency with the laws of thermodynamics. Three-dimensional FEM calculations are presented showing anisotropic effects.

Development of Microstructure during Mechanical Alloying of Ni-Cr-Alloys

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Dr. Thomas Steffens

Dr. Klaus Zöltzer

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Mechanical alloying is a convenient method to produce heterogeneous alloys with a fine dispersion. High energy ball mills, e.g. attritors and centrifugal vibration mills are especially effective to exercise this process.

Mechanical alloying is a complex process comprising among other steps simultaneously and competing

- crushing of brittle constituents
- rolling out ductile constituents into thin flakes
- crushing these flakes
- cold rewelding particles, thereby occluding other constituents
- re-crushing of rewelded agglomerates

This poster shows how mechanical alloying process can readily be followed by optical microscopy and X-ray diffraction.

U. Zwicker, U. Holzwarth  
Lehrstuhl Werkstoffwissenschaft (Metalle), Universität  
Erlangen-Nürnberg

Production of Materials with Low Elastic Modulus by Sintering  
of Titanium Alloys

Implant materials of titanium alloys with an elastic modulus of the same dimension as the human bone can be achieved by sintering of powders for example Rotating Electrode Process powder to a density which is adequate to an elastic modulus of about  $10.000 \text{ N/mm}^2$  which is approximately corresponding to the elastic modulus of the bone<sup>1)-3)</sup>. Whilst up till now the alloy TiAl5Fe2.5, which consists of components which are all biocompatible, was used new alloys with biocompatible components are in development which have in the compact state an elastic modulus lower than that of TiAl5Fe2.5 so that the porosity of the sintered powders can be diminished and by that the mechanical strength is increased.

- 1) U. Zwicker, Metallkundliche Untersuchungen an der Implantatlegierung TiAl5Fe2,5, Zeitschrift für Metallkunde Bd. 77 (1986) H. 11, 714-720
- 2) U. Zwicker, J. Breme, U. Etzold, Poröse Titanwerkstoffe mit niedrigem E-Modul aus gesintertem Titanlegierungspulver, 7. Vortragsreihe des DVM-Arbeitskreises "Implantate" und der Deutschen Sektion der AO-International, 18.11.1986, Berlin, S. 47-58
- 3) J. Breme, V. Wadewitz, Th. Mayr, Optimierung der mechanischen Eigenschaften poröser Sinterkörper aus der Implantatlegierung TiAl5Fe2,5 mit dem Ziel der Herstellung von Zahnimplantaten, Zeitschrift für Zahnärztliche Implantologie, Band III (1987) 41-46

# BOROSILICIDING OF AUSTENITIC STAINLESS STEELS

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In order to obtain hard and wear resistant surface coatings, some austenitic stainless steels differing in nickel content were treated at 1123 K with powder media containing both B and Si compounds.

The coatings were characterized by means of X-ray diffraction, electron probe and metallographic analyses. The results were compared with those obtained by treating iron and nickel samples under the same processing conditions.

The conditions allowing the growth of borides, silicides or both were investigated. The possibility of a controlled transformation of iron borides into iron silicides during the treatment was pointed out, and a reaction mechanism proposed.

**SUPERPLASTICITY OF HIGH STRENGTH ALUMINUM ALLOYS**

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Aluminum alloys AA 7012, AA 7075 and AA 7475 were subjected to thermo-mechanical processing sequences in order to obtain a ultrafine-grained microstructure; then superplastic tension tests were performed. The superplastic flow characteristics were studied at 790 K by means of a step/strain rate test, determining the log-log curves of flow stress as a function of strain rate and the strain rate sensitivity for each rate value. The fracture surfaces were examined by SEM microscopy. The observations have confirmed the Gifkin's model; the deformation mechanism of the grain mantle is prevailing in a fine grained material during the superplastic forming.

The formability of the alloys is controlled by the coalescence of microvoids leading to a premature failure. The loss of mechanical properties occurs for elongation values higher than ~300% in the case of 7075 and 7475 alloys, ~150% for the 7012 alloy.